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IN ENGLISH TRANSLATION

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COMPLEXONES AND THEIR SIGNIFICANCE IN ANALYTICAL CHEMISTRY

S. I. Sinyakova

The V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry

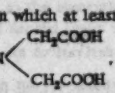
USSR Academy of Sciences, Moscow

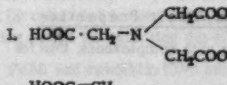
A new class of complexing agents called "complexones" have, in recent years, found wide application in chemistry, particularly in analytical chemistry.

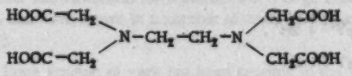
As a result of their exceptionally interesting property of forming extremely stable, soluble complexes with many cations, complexones have opened up new possibilities for the solution of a number of analytical problems.

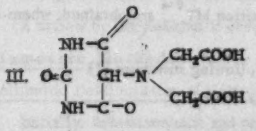
Complexones can be used technologically for the isolation of rare elements and others, e.g., the rare-earths on ion-exchange columns [1], for softening water for printing, in dye-stuffs, for working with colored cine-films, etc..

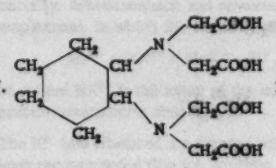
Many patents have appeared in the last twenty years devoted to the application of complexones in various branches of the chemical and pharmaceutical industries and others.

Complexones are amino-polycarboxylic acids and their derivatives, in which at least 2 acetic acid residues are linked with nitrogen. Their characteristic group is imino-diacetic acid  , in which the hydrogen of the imino group can be replaced by organic radicals, as a result of which the following compounds are formed:

I.  Nitrilotriacetic acid (complexone I)

II.  Ethylenediaminetetracetic acid (complexone II)

III.  Uramyl-N-N-diacetic acid

IV.  1,2-Diaminocyclohexane-N,N,N',N'-tetracetic acid (complexone IV)

and other derivatives.

The disodium salt of complexone II was issued by the chemical industry in 1936 under the trade name "Trilon B"; it is often called "complexone III", while complexone I and its salts are issued under the name Trilon A.*

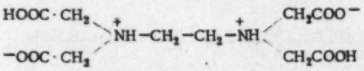
* Our chemical industry turns out 2 reagents, Trilon A and Trilon B.
In American literature, Trilon B is called "versene", "sodium versenate", "versenic acid", "sequestrene", while complexone II is shortened to EDTA.

Chemical and Physico-Chemical Properties of Complexones

Complexones are solids which are sparingly soluble in water. Dissociation constants have been determined for many complexones, e.g., the values found for complexone II, expressed as the inverse logarithms are as follows:

$-\log K_1$	$-\log K_2$	$-\log K_3$	$-\log K_4$
1.996	2.672	6.161	10.262

It is obvious that only 2 out of the 4 protons in complexone II have a strongly acidic character, which indicates a double betaine structure [2]



On neutralization of this acid, which we denote by H_4Y, initially 2 protons split off

$$H_4Y = H_2Y^{2-} + 2H^+ .$$

The H_2Y^{2-} anion thus formed also has acidic properties and on further neutralization another proton is released

$$H_2Y^{2-} = HY^{3-} + H^+$$

and further

$$HY^{3-} = Y^{4-} + H^+ .$$

Complexone I and its derivatives are strong uni-proton acids [3].

Descriptions of the methods used for preparing the various complexones have been given [4]. New complexones have been synthesized in the Soviet Union [5].

The Complexes Formed between Metals and Complexones, and Their Properties

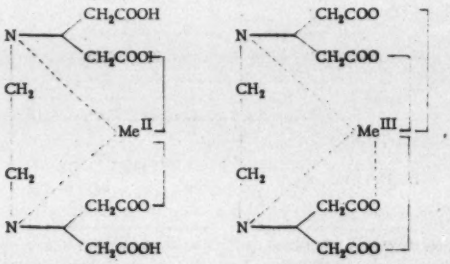
Complexes (which are soluble in water) are formed when some cations react with complexones; thus for complexone II, e.g., we get the reaction

$$Me^{2+} + H_2Y^{2-} = MeY^{2-} + 2H^+ ,$$

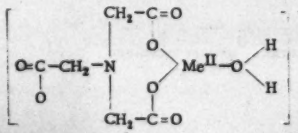
$$Me^{3+} + H_2Y^{3-} = MeY^{-} + 2H^+ .$$

In the general case, when complexone II is used, complexes of the composition MY^{V-4} are obtained, where M^{V+} is the cation, and Y^{4-} is the anion of the acid.

According to Schwarzenbach, these complexes can be represented by the following structures [6]:



while for the complexes formed between complexone I and divalent cations, the following structures have been suggested [7]:



Similar structures which contain combined water or some other addends are formed by metals with other complexones, since their central atom has a free coordinate bond which is capable of coordinating such addends as CNS, Br, Cl, NO_2, etc.. This has permitted a series of new cyclic complexes with CoY^{2-} to be isolated [6].

Many metals (Ca, Mg, Al) form hydroxy complexes, with the composition $MeOHY^{III}$, which are intermediate products.

Moreover, in acid solutions, complexes of the type $[MeHY^{-}]$ [2], are formed as intermediates.

Thanks to the work of Schwarzenbach and coworkers, and other research workers [8], the structures of many complexes formed between metals and complexones have been studied, as well as their instability constants, and the kinetics of formation of these complexes.

Koryta and Kössler have determined the instability constants of many complexes formed with complexone I polarographically [9].

Schwarzenbach and coworkers, in the same way, have determined the instability constants of 49 complexes formed by complexones II and IV.

It follows from the values of the instability constants adduced by them, that these complexones form very stable complexes with a number of metals; complexone II forms particularly stable complexes with Fe^{III}, In, Sc and Th, for which: $-\log K_{\cdot} = 25.1$; 24.95; 23.1; 23.2 (respectively). The alkaline-earth elements also form very stable complexes with it: $-\log K_{CaY} = 10.96$; $-\log K_{MgY} = 8.69$ [10]. The complexes formed by the alkali and alkaline-earth elements with aniline-diacetic-o-carboxylic acid are also fairly stable [11].

The complexes of Fe^{III} and Fe^{II} with complexone I [12], and II [13], the complexes of the rare-earths with Trilon A and B [14], and others have been fairly thoroughly studied, as well as the absorption spectra of the latter [15]. Astakhov and Kiseleva [16], have studied the properties of the complexes of second group metals with Trilon B.

Complexones in Chemical Analysis

Many complexones, in particular complexone III (Trilon B) have been widely applied in various branches of analytical chemistry. They can be used directly in analytical chemistry, as standard solutions for titration, or as reagents for colorimetric determinations, or complexing agents displacing oxidation-reduction potentials, and also as masking agents for inhibiting the effect of interfering elements.

Pribil and coworkers have carried out a large amount of work on the application of complexones in chemical analysis, and have shown in a number of cases how much simpler it is to carry out analysis in the presence of complexones [17].

A large amount of work has been devoted to the use of complexones in volumetric and polarographic analysis.

A review by Goryushkina is devoted to the use of Trilon B in analytical chemistry [18].

Volumetric Methods

Alkalimetric Determination of Cations

Initially, Schwarzenbach and coworkers developed indirec alkalimetric methods for the determination of metals with complexones, in which the capacity of the metal to expel the H^+ ions from a complexone by the reaction

$$Me^{2+} + HX^{2-} = MeX^{-} + H^{+}, \quad (1) \qquad Me^{2+} + H_2Y^{2-} = MeY^{2-} + 2H^{+}, \quad (2)$$

was used, where HX^{2-} is the anion of the salt of nitrilotriacetic acid K_2HX, while H_2Y^{2-} is the anion of the salt of ethylenediaminetetracetic acid K_2H_2Y.

The H^+ ions liberated are titrated with alkali in the presence of the usual indicators (or potentiometrically) [19]. It has been recommended that the hardness of water (Ca + Mg) [20], and also other metals (Cu, Fe, Co, Pb, Cd) [19] be determined in this way.

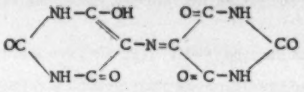
Another variant of the determination of water hardness is based on direct titration with an alkaline solution of complexone II [22].

Methods involving direct titration of the cations with complexones in the presence of special indicators [23-25], have, however, found much wider application.

Direct Complexometric Titration

In the case of direct complexometric titration, indicators are used which form an intensely colored complex with the given cation; this complex is, however, less stable than the corresponding complexes formed between the

same cation and the complexone, as a result the latter takes the cations from the cation indicator complex. At the equivalence point, i.e., when all the cation has been complexed by the complexone, the color of the free indicator appears; this color differs from the color of the cation-indicator complex. Such an indicator, e.g., is murexide (ammonium purpurate)



which forms a complex with calcium ions as follows

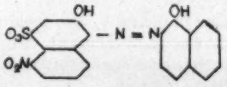
$$\underset{\text{bluish-violet}}{Ca^{2+} + J^-} = \underset{\text{red}}{CaJ^+},$$

where J^- is the murexide anion. On titrating wich complexone II, when the equivalence point is reached, the CaJ complex breaks down to give free murexide anions according to the reaction [26]:

$$\underset{\text{red}}{CaJ^+} + H_2Y^{2-} = \underset{\text{bluish-violet}}{CaY^{2-}} + 2H^+ + J^-.$$

This method has been particularly widely used for the determination of calcium and magnesium, but more than 15 cations and some anions (indirectly) can be determined as well.

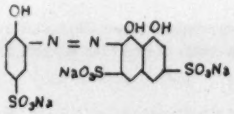
Murexide is used for titration of Ca, Cu, Ni, while Eriochrome black T* is used for titrating Mg, Zn, Cd, Mn, In, and others [27].



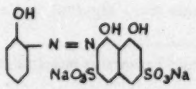
a) Determination of Calcium and Magnesium

Complexometric determination of calcium and magnesium is so simple and rapid, that this method is now predominantly used for the determination of these elements in water and in various products.

Complexometric titration is particularly widely used for the determination of water hardness. Murexide and eriochrome-Black-T [28, 29, 30] are used as indicators. Nevertheless, other indicators have been suggested for this purpose, e.g., acid chrome blue K



and acid chrome dark-blue,



which are more sensitive than Eriochrome-Black-T [31].

* This is supplied in the Soviet Union under the trade name "Chromogen Black Special ET 00".

Lure and Nikolaeva [32], have proposed two new indicators for the determination of the hardness of natural and softened water: 8-hydroxyquinoline and titanium yellow.

It has also been shown that water hardness can be determined by complexometric titration (Trilon B) in the presence of a number of elements (Cu, Zn, Mn, Fe, and Al), if Cu and Zn are precipitated as sulfides and the solutions diluted accordingly. The presence of a precipitate does not interfere with titration [33].

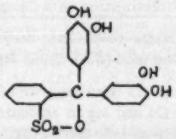
The same method has been applied by Fesenko [34], for determining calcium in water, using murexide* as indicator, and by Arkhangelskaya [35] for determining magnesium in the presence of calcium, which is precipitated first as oxalate.

A considerable amount of work has been published on the determination of calcium and magnesium in various materials by complexometric titration, e.g., in soils and plants [36], in limestones and dolomites [37, 38], in coal ash and in fire resistant materials [39], in marine salts and in lacs [40], in pharmaceuticals [41], in blood plasma [42], and in other materials, and also calcium in magnesites [43], in blood [44, 45], etc..

b) Determination of Other Elements

It has been shown that barium can be determined complexometrically [46, 47].

By titration with Trilon B, it is also possible to determine Fe, Cu, Co, Ni, Cd, Pb, Zn, In, Al, Th, Bi, Ca and other cations, which form stable complexes with it, for many of these cations special indicators are used, e.g., for Fe^{III} it is possible to use thiocyanate or sulfosalicylic acid as indicators [48, 49], for thorium, Alizarin S [25], for bismuth and thorium



pyrocatechol violet [50, 51], etc..

Bismuth and thorium can be determined with pyrocatechol violet as indicator in the presence of excess lead, and other cations (Cd, Cu, Zn, Co, Ni, Mn, Ca and Mg).

Iron. For a better color change at the end point during titration of Fe^{III} with thiocyanate, it is recommended that a small amount of ether be added for extracting the colored thiocyanate complex of Fe. Iron can be determined in the presence of aluminum or zinc, if citrate is added to the solution being titrated [49].

Indium can be determined by complexometric titration of its hot solution containing tartrate, and Eriochrome Black T as indicator. Some cations can be prevented from interfering with indium determination by masking them with KCN [Hg, Cu, Cd, Co, Zn, Ni, Fe^{III}].

The alkali metals do not interfere either, or Tl, Ag, As, Sb, Sn^{IV}, CrO_4^{2-}, WO_4^{2-}, MoO_4^{2-}.

The elements which interfere are those that form stable complexes with Eriochrome Black T (Al, Ti, Bi) and also Mn, Pb and the alkaline earth elements [52]. Interference from Fe^{III} during complexometric titration of In and others (Ca, Mg, Pb, Mn, Zn) in the presence of Eriochrome Black T can be eliminated by reducing the Fe^{III} to Fe^{II} with ascorbic acid and complexing the ferric salt with KCN [53].

Thorium can be determined by direct titration with Trilon B from buffered solutions, using Alizarin S as indicator [25, 54]. Thorium reacts with Trilon B as follows:

$$Th^{4+} + Na_2H_2Y \rightleftharpoons ThY + 2H^+ + 2Na^+.$$

Since Th^{4+} gives a very stable complex with Trilon B at low pH (2.4-4.8), the solutions of its salts are very suitable as titrant for the determination of other cations by complexometric titration [55]. For example, determination of Ni, Bi, and Al is based on back titration of excess Trilon B with a solution of $Th(NO_3)_4$.

* This paper contains details of a method for preparing murexide from uric acid.

Zirconium. In compounds with uranium, Zr^{IV} is first precipitated with mineral acid, then after dissolving it, it is complexed with Trilon B, and excess of the latter back titrated with $FeCl_3$ using salicylic acid as indicator [56].

Cadmium and magnesium can be determined when they are present in solution together, if titration is carried out with Zn-complexonate* using Eriochrome Black T as indicator.

In this case we have an interesting reaction in which Zn^{2+} is displaced from its complexonate and the Zn^{2+} ions themselves used as the indicator. Cd^{2+} is titrated at a pH of 6.8, while Mg is titrated at pH 10. Cd^{2+} can be determined in the presence of 50 times its amount of magnesium. Ca^{2+}, Pb^{2+}, and Zn^{2+} interfere [57].

Zinc and uranium. For the analysis of zinc-uranium alloys which contain ca 80% Zn, and ca 20% U (or 0.3-0.4% Zn), zinc is determined by titration of excess Trilon B with $ZnCl_2$ using murexide as indicator. Uranium is kept in solution by adding $NaHCO_3$ [58].

Extremely interesting possibilities are opened up by the use of 2,3-dimercaptopropanol $CH_2(SH)-CH(SH)-CH_2(OH)$ (I) as a masking agent for complexometric titrations. For example, it permits determination of Ca and Mg in the presence of Pb and Bi. By using the differing reactivities of the complexonates with respect to (I), it is possible to determine cations in mixtures, e.g., Pb in the presence of Mn; Zn in the presence of Ni, etc.. By combining (I) with other complexing agents (KCN, triethanolamine) or applying selective precipitation, it is possible to determine Pb, Co, and Mn, or Pb, Zn, Ni, Mg, and Ca in the presence of Fe and Al. As a result a series of elements can be determined simultaneously in alloys, ores, and in other materials [59].

Microtitration with Complexones

Flaschka [60], has worked out a number of micro-volumetric methods of determining some elements by titrating with Trilon B, dilute solutions of Trilon B being used (0.01-0.001 N).

Cadmium, magnesium and others. A method has been suggested for the microtitration of Cd, Mg, and Zn and others. By this method it is possible to determine Cd and Mg in amounts of 8-12 μg, and Zn in amounts of 1.5 μg, when titration is carried out with a Trilon B solution of $1-5\cdot10^{-4}$ M [61].

Lead can be determined by microtitration when it is present in a few micrograms, when titration is carried out in the presence of tartaric acid in a buffer solution with a pH of 8-10 using Eriochrome Black T as indicator. Zn, Ni, Cu and others can be masked by means of cyanide [62].

Indium and manganese in micro amounts can be titrated directly with Trilon B, if titration is carried out in a tartrate-ammonium solution using Eriochrome Black T indicator. Heavy metals are masked with KCN; if it is also necessary to determine Zn and Cd, they can be "demasked" from their cyanide complexes by addition of formaldehyde and also titrating with Trilon B [63].

Thallium (I) in small amounts is determined by a back titration of excess Mg-complexonate in the presence of Eriochrome Black T as indicator [64].

Iron (III) in amounts up to 20 μg can be determined by direct titration with Trilon B in the presence of a redox indicator: variamine blue B (4-amino-4'-methoxy-diphenylamine) [65].

Copper can be determined by direct titration with Trilon B using murexide indicator.

Nickel and cobalt can also be titrated directly in small amounts with Trilon B using murexide as indicator [60].

Aluminum and thorium can also be determined by complexometric titration in micro amounts [67].

Indirect Methods of Determining Certain Elements by Complexometric Titration

Methods have also been developed for indirect complexometric determination of a number of elements.

Sodium, e.g., in amounts less than 20 μg can be determined with an accuracy of 2-3%, if it is precipitated as Na-Zn uranyl acetate and after the precipitate has been dissolved, the Zn titrated with Trilon B, using Eriochrome Black T as indicator [68].

Phosphate ion (PO_4^{3-}) can be indirectly determined, by precipitating it as $MgNH_4PO_4$, and the magnesium then titrated with Trilon B [69].

* We shall call the complexes formed between metals and complexones – complexonates.

Cyanide ions (CN^-) are determined by titration of excess Ni^{2+} with Trilon B after its precipitation with an ammoniacal solution of a nickel salt. Murexide is the indicator [70].

The tungstate ion (WO_4^{2-}) is precipitated as calcium tungstate and after working up with HCl, Ca^{2+} is titrated with Trilon B. The method has been applied to the determination of tungsten in minerals [71].

The sulfate ion. For the determination of sulfate, excess of Ba^{2+} ions are added and excess titrated with a complexone using Eriochrome Black T as indicator [72].

Some indirect methods for the complexometric determination of elements which are not titrated by complexones themselves are based on displacement of other ions from their complexes and subsequent determination of these ions by titration with complexones. For example, determination of Pd^{2+}, Cl^-, Br^- and others.

Palladium. Palladium determination is based on displacement of Ni^{2+} from $K_2[Ni(CN)_4]$ according to the reaction

$$[Ni(CN)_4]^{2-} + Pd^{2+} = [Pd(CN)_4]^{2-} + Ni^{2+}$$

and titrating the displaced Ni^{2+} with Trilon B and murexide in ammoniacal solution [73].

Chlorine, bromine, iodine. Determination of halogen has also been based on displacement of Ni^{2+} ions from $Ni(CN)_4^{2-}$ by means of Ag^+

$$Ni(CN)_4^{2-} + 2Ag^+ = 2[Ag(CN)_2]^- + Ni^{2+}$$

the Ni^{2+} ions expelled being then titrated with Trilon B and murexide. Cl^-, Br^-, and I^- are precipitated as AgCl, AgBr, or AgI and dissolved in ammonia [74].

Examples of Determination of Various Components in Different Products by Titration with a Complexone, or by Other Reagents in the Presence of a Complexone

Zinc can be determined in lithopone (ZnO + ZnS), and lead in ZnO by titration with a complexone in the presence of tartaric acid [75].

Nickel in steel. In this case nickel is precipitated with Na-diacetyldioxime in citric acid solution, the precipitate dissolved in HCl, and the Ni^{2+} titrated with Trilon B using murexide as indicator [77].

Calcium in phosphorites. Phosphate is first of all isolated by precipitation on an ion-exchange column, and the Ca^{2+} then titrated with Trilon B using a mixed indicator of: Eriochrome Black T and Methyl yellow. In the presence of magnesium, excess Trilon B is added, which is then back titrated with $Ca(NO_3)_2$ + murexide, dissolved in anhydrous ethylene glycol (for increasing the stability of the solution) [78].

Zinc. Zinc can be determined in magnesium and its alloys by complexing Zn^{2+} with CN^- and passing the solution through Amberlite IR-120. The magnesium is thereupon precipitated on the cation exchange resin, while the zinc complex remains in solution. Zn^{2+} is "demasked" by adding formaldehyde and titrated at a pH of 6-8 with complexone III [79].

Boron can be determined in glass by acidimetric titration of the complex of boric acid with glycerol or mannite in the presence of complexone III which complexes Pb, Zn, Mn, Fe, Al, Ca, Mg and other metals contained in the glass to give stable complexes [80].

Complexometric Titrations in which the Equivalence Point is Determined by Means of a Spectrophotometer

New possibilities have been opened up for the application of complexones in volumetric analysis by using a spectrophotometer to establish the equivalence point.

Iron, copper and nickel. These cations can be determined when present simultaneously in solution, if the salicylate complex of Fe^{III} is titrated with Trilon B at 525 mμ, that of Cu at 745 mμ and that of Ni at 1000 mμ. Fe can be determined in iron alloys and Cu in non-ferrous alloys by this method [81].

Iron and copper, or bismuth and copper can be determined by titration with Trilon B using a spectrophotometric method of determining the equivalence point [82].

Ca, Mg, Cd, Zn, Ti, Zr. Ca + Mg or Cd + Zn can be determined by titration with Trilon B solution at a pH of 10; absorption is measured at 222 mμ or 228 mμ. On addition to the solution of NaOH + citric acid and KCN it is possible to determine Ca in the presence of Mg. Cd can also be determined in the presence of Zn. Titanium can

be titrated with Trilon B at 450 mμ or in the presence of H_2O_2 at 520 mμ (pH 1.9). The accuracy of the method is ± 1% [83].

Patrovsky's method of determing Ga and In is of this type.

Gallium and indium. Both of these elements give an intense green fluorescence with morin in the ultraviolet, which gradually extinguishes on titrating with Trilon B. Other cations do not interfere. Small amounts of Fe^{III} and Al can be masked with a fluoroborate, fluorosilicate, or fluoride. Methods for the determination of gallium in aluminum and in bauxites, and of indium in sphalerites are based on this principle [84].

Complexones as Masking Agents in Iodimetry

The masking properties of complexones are also used in iodimetry. In the presence, e.g., of Trilon B, Cr^{VI}, Ce^{IV}, and Mn^{VII} do not react with I^-. Iodometric methods of determining these oxidizing agents in the presence of Fe^{III} and Cu^{I} are based on this fact. Initially, all the ions are reduced with iodine, and then the Fe^{II}, and Cu^{I} complexed into stable complexes with Trilon B. The complexonates of Ce^{III}, Mn^{III} and Cr^{III} formed are instantaneously oxidized by free iodine and excess of the latter titrated with $Na_2S_2O_3$ [85].

"Demasking" during Complexometric Titration

"Demasking" reactions also play an important part in volumetric complexometric methods as well as masking ones. For example, Cu, Zn, Cd, Ni, Co and others are first combined into cyanide complexes and then the cyanide complexes $Cd(CN)_4^{2-}$ and $Zn(CN)_4^{2-}$ are "demasked" by addition of formaldehyde or chloral hydrate, and the freed Zn^{2+} and Cd^{2+} ions titrated with a complexone. By this means Cd and Zn can be determined in the presence of Cu, Ni, and Co.

Determination of Zn in aluminum alloys and ores is based on the same principle, after precipitation of zinc as dithiocarbamate, extraction of the latter with ethyl acetate and then displacement from the organic phase [86].

Selective Precipitation Methods during Complexometric Titration

Selective precipitation methods are also used during complexometric titrations. For example, when Bi and Zn, or Bi and Cd are being determined simultaneously, their sum is first determined by a back titration of excess Trilon B with $MgSO_4$, and then another part of the solution of Cd and Zn is titrated after precipitation of Bi and BiOCl. When Cd and Zn, or Pb and Zn are being determined simultaneously, first the sum of both ions is determined by direct titration with Trilon B, afterwards Cd or Pb is precipitated from weak ammonia solutions with Na-dithiocarbamate and the liberated complexone, equivalent to the Cd or Pb content, titrated with $MgSO_4$. Zinc is determined by difference [86].

Colorimetric and Spectrophotometric Methods

Certain trivalent metal ions form colored complexes with Trilon B, on the basis of which colorimetric methods can be developed for determining them.

Chromium. In weakly acid media, on heating, Cr^{III} gives a violet-red color with Trilon B. It is possible to determine chromium quantitatively if the extinction is measured at 550 mμ. This method is used for the determination of chromium in steel [87]. Kuznetsov has shown that the color of Cr^{III} with complexone I depends on pH; this is explained in his opinion by a decrease in intramolecular dissociation and by simplification of the complex composition [76].

Silver can be determined in ores colorimetrically with n-dimethylaminobenzalrhodamine in the presence of complexone III [66].

Cobalt. Co^{III} gives a violet color with Trilon B, the intensity of which can be determined by means of a colorimeter with a green filter at 540 mμ. Co^{II} must first be oxidized to Co^{III}, e.g., by means of H_2O_2 in a weak acid medium [88].

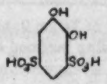
Manganese. Trilon B gives an intense red color with Mn^{III} which can be also be measured in a colorimeter fitted with a green filter.

By using a differential photocolorimeter it is possible to determine Cr, Co and Mn on one aliquot [89].

Complexones are used in colorimetry as masking agents. For example, dithizone can be used as a selective reagent for mercury, if the mercury dithizonate is extracted in the presence of complexone III and KCNS [90].

Copper can be determined colorimetrically as dithiocarbamate in the presence of Ni, Co, Mn, Fe and others if the complex is extracted with ethyl acetate in the presence of Trilon B. Using this method, copper has been determined in steels, alloys, ores and in salts of Ni and Co [91].

Cobalt II. In the case of determination of Co with dithiocarbamate Trilon B in conjunction with thyron



KCN, etc., has been used as a masking agent Determination of cobalt in steel [92] and also in nickel and nickel salts [93], has been carried out on this basis.

Beryllium. During spectrophotometric determination of Be as the sulfosalicylic acid complex at 317 mμ, the effect of other elements can be eliminated by adding complexone III. Be can be determined in aluminum by this method:[94].

During the colorimetric determination of Be as a complex with aluminon, addition of Trilon B eliminates interference from Cu, Al, Zr, Ti, Mn, Fe, Ni, Co and Zn.

The method is suitable for the determination of Be in copper-beryllium bronzes [95].

Uranium. Spectrophotometric determination of uranium as the complex with dibenzylmethane, after extraction with an organic solvent in the presence of Trilon B, allows uranium to be determined in the presence of other elements in the test sample [96].

Nitrates. Colorimetric determination of nitrates with phenoldisulfonic acid can be carried out in the presence of Ca and Mg, if the turbidity which results from their presence is removed by addition of complexone II. Nitrates can be determined by this method in water, in soil extracts, etc. [97].

Gravimetric Methods

Gravimetric methods of determining elements by means of complexones are based on the varying stabilities of the complexonates of the different metals. This property allows one to separate, by means of ordinary precipitants, elements which form comparatively weak complexes, while other elements forming more stable complexes are not precipitated, i.e., the complexones are used in this instance as masking agents. For example, only U, Be, Tl, Sn^{IV}, and Sb^{III} are by precipitated by NH_3 in the presence of complexone III, while Fe, Al and others are not precipitated. A number of gravimetric methods have been worked out for the determination of these cations, and indirectly of some anions.

Precipitation with Ammonia

Beryllium can be determined gravimetrically as BeO after precipitation with NH_3 in the presence of Trilon B, which prevents precipitation of other metals (Fe, Al, etc.) . The method has been applied for the determination of Be in aquamarines [98], and in bronzes [99].

Beryllium can be determined by precipitation as the pyrophosphate in the presence of complexone III. The method has been applied for the determination of Be in beryls [100].

Titanium. Gravimetric determination of titanium as TiO_2 in bauxites, ferrotitanates, and in clays is based on the same principle [101].

It is also recommended that during the separation of small amounts of titanium from large amounts of iron and other cations during its spectrophotometric determination by H_2O_2, Ti be precipitated with NH_3 in the presence of Trilon B. It is necessary to oxidize Cr^{III} beforehand to Cr^{VI} [102].

Uranium can also be separated from Fe, Al, Pb, Bi, Cr, Ni, Co and others, by precipitating it with ammonia in the presence of Trilon B [103].

Uranium, Titanium and Beryllium. A method has also been proposed for the simultaneous determination of U + Tl + Be in the presence of Fe, Al, Bi and other metals, by precipitating with ammonia in the presence of Trilon B, followed by separation of Tl with $(NH_4)_2CO_3$, and then separation of Be from uranium with ammonia from oxalate solution [104].

Precipitation with $(NH_4)_2S$

Many cations, which are normally precipitated with $(NH_4)_2S$ are not precipitated in the presence of complexones. For example, Zn^{2+} Mn^{2+}, Co^{2+} and Ni^{2+} are not precipitated in the presence of complexone III, while Hg^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, and Bi^{3+} are precipitated with $(NH_4)_2S$. From a solution containing complexone I, only Zn^{2+} is precipitated

with $(NH_4)_2S$. Ni^{2+} and Mn^{2+} are not precipitated. This allows these elements to be separated [105].

Precipitation with 8-Hydroxyquinoline

At known pH values, it is possible, in the presence of Trilon B, to precipitate only U, Mo, W and Ti, with 8-hydroxyquinoline. Using Trilon B + tartaric acid in alkaline buffered solutions ensures precipitation of only U, Fe, Al, Cu, Ti and Be by 8-hydroxyquinoline. This permits development of a method for the determination of Mo, Cu, Fe and U when they are present together, and also of Mo and W on precipitation of the latter with 8-hydroxyquinoline from weakly acid solutions [106]. Molybdenum has been determined in Wulfenites and ferromolybdates [107].

Displacement Methods

Some gravimetric methods of determining cations are based on their quantitative displacement from their complexonates byother cations, which form more stable complexes with the complexone, than the cations they displaced. Gravimetric determinations of Bi, Fe, Al and others are basedon this principle.

Bismuth is not precipitated by NH_4OH from solutions containing complexone III, but it can be quantitatively precipitated as $Bi(OH)_3$ on addition of Ca^{2+} to the solution, which displaces Bi according to the reaction

$$BiY^- + Ca^{2+} + 3OH^- = Bi(OH)_3 + CaY^{2-}.$$

The application of such a method permits bismuth to be separated from lead, so that a technique can be worked out for the determination of bismuth in low melting alloys and in lead [108].

Cobalt. The same principle serves as a basis for separating cobalt and nickel, since in alkaline media Ca^{2+} displaces Co^{2+}, Zn^{2+}, and Mn^{2+} from their complexonates, but not Ni^{2+}. In the presence of sulfide, Co^{2+}, Zn^{2+} and Mn^{2+} are quantitatively precipitated as sulfides according to the reaction:

$$MeY^{2-} + S^{2-} + Ca^{2+} = MeS + CaY^{2-},$$

while Ni^{2+} remains in solution [109].

Zinc. From a solution containing complexone I, Ca^{2+} only displaces Zn^{2+}, while Ni^{2+}, Mn^{2+}, and Co^{2+} are not displaced. This means that a method can be developed for the determination of zinc as ZnS (not containing even traces of Ni^{2+} and Mn^{2+}), which would be applicable for the determination of Zn in alloys [109].

Molybdenum. A method of separating molybdenum from iron and Group 3 cations by means of H_2S is based on the same principle [99].

Flaschka investigated the possibility of separating certain cations by displacing them from their complexonates with Ca^{2+} and then precipitating them with thioacetamide [110].

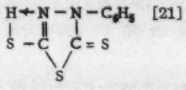
The masking role of complexones during precipitation reactions is also being widely used.

Calcium, for example, can be quantitatively precipitated as oxalate in the presence of complexone III. Pb, Cu, Cd, Bi, Hg, Fe, Al, Cr, As, Sb, Ti, Be, U, Mo, W, Zn, Co, PO_4^{3-} and others do not interfere.

This method has been used for determining calcium in lead-calcium alloys and in minerals [111].

Thallium (I) can be quantitatively precipitated by KI. Fe^{III}, Cu^{2+}, Pb^{2+}, Bi^{3+} and others which form stable complexes with complexone III do not interfere [112].

Mercury. In the presence of complexone III and Rochelle salt, mercury can be quantitatively separated from Sb, Sn, Bi, Ti and others by precipitation with mercaptophenyldithiodiazole [21]



[21]

The phosphate ion (PO_4^{3-}) can be determined in the presence of Pb, Cu, Cd, Bi, Al, Fe, Ti, Be, U, Sb, Sn, Ca, Sr and Ba by precipitation as NH_4MgPO_4 in the presence of complexone III and thyron [69, 113].

This method has been used for the determination of phosphorus in apatites and polymorphites [114].

Barium can be quantitatively separated from Pb and other cations, if precipitation by sulfate is carried out in the presence of complexone III. SO_4^{2-} is also precipitated by Ba^{2+} ions in the presence of complexone III and can be determined in the presence of Fe, Al, Cr, Cu, Ni, and Co.

This is a convenient method for determination of sulfur in sulfides [115].

Polarographic Methods

Polarographic methods have proved very effective for studying the structure of complexes formed by complexones, for determining their instability constants, and for quantitative determination of some elements. In the presence of complexones, the half-wave potentials of many cations, as a result of the formation of stable complexes, are shifted to more negative potentials, in particular, the $E_{1/2}$ for Ni, Co, Zn, and Mn are more negative than $E_{1/2}$ for ammonium NH_4^+, so that new possibilities have arisen for the determination of cations present simultaneously in solution.

By means of polarographic methods, complexes of europium and complexone III have been investigated [116]. The kinetics of formation of the complexonates formed between Cd, Pb, and Zn with complexone I has been studied, and their instability constants determined (with a streaming mercury electrode) [9]. Complexes of vanadium (II, III, IV, and V) with complexone III [117], of titanium and complexone III [118, 119], have been studied, as well as the complexes formed between hexamethylenediaminetetracetic acid and the disodium salt of benzylaminediacetic acid and many metals [5], and the complex HgY^{2-}, for which the instability constant is $10^{-22.8}$ [120]. It has been shown that FeY^- is reduced to FeY^{2-}, by combining with one electron [13].

The reactions, which have been studied polarographically, and in which cations are displaced from complexonates by other cations, forming more stable complexes, are of great practical interest. This has allowed new polarographic methods to be worked out for the determination of ions which are not usually determined polarographically. For example, the high displacement rate of Zn^{2+} and Co^{2+} from their complexonates (with Trilon B) in 4 N NH_4OH according to the reaction $MeY^{2-} + Ca^{2+} \rightleftarrows CaY^{2-} + Me^{2+}$ (where Me = Zn or Co), as compared with the rate at which Ni^{2+} is displaced has suggested a polarographic method of determining Zn and Co in nickel and its salts [121].

By using complexones in polarographic analysis, it is also possible to determine simultaneously metals which usually interfere with one another. This can be demonstrated by the following examples.

Iron, copper and cobalt. Iron can be determined in a Trilon B solution using sodium acetate as supporting electrolyte, in the presence of 100 times its own amount of copper, while copper can be determined under the same conditions in the presence of an equal amount of iron. Both metals can, thereby, be determined separately. Cobalt can be determined in the presence of Cu and Ni, if the cobalt is oxidized to Co^{3+} and the latter then determined polarographically using the potassium salt of complexone III + pyridine + pyridine hydrochloride as supporting electrolyte. Fe^{III} does not interfere either, since it is precipitated by the pyridine. Cobalt has been determined by this method in melts [122].

Copper, bismuth, iron. These three cations can be determined simultaneously by using complexone II in a supporting electrolyte of potassium citrate and $(NH_4)_2CO_3$ [123].

Thallium (I). Of particular interest is the behavior of thallium, for which $E_{1/2} = -0.46$ V (with respect to the saturated calomel electrode) at all pH's in the presence of a number of complexing agents (citric, tartaric acids, etc.), this fact interferes with its determination in the presence of Pb and Sn (in acid solutions), Pb and Cu (in alkaline solutions). On addition of complexone III, the waves of Tl, Pb, and Cu are shifted with respect to each other, so that a method can be worked out to determine Tl in lead and in biological materials [124].

Molybdenum. The complex of Mo with complexone III is easily reduced from weakly acid solutions and $E_{1/2} = -0.63$ V (saturated calomel electrode). Tungsten is not reduced under these conditions, so that it is possible to determine traces of Mo in tungsten. Many di- and tri-valent metals such as Pb, Fe, and Cu do not interfere. Only Tl and Bi interfere. Mo has been determined in ores by this method with satisfactory accuracy [125].

Germanium (IV) gives a well-defined wave at -1.3 V in the presence of complexone III when $NH_4OH + NH_4Cl$ is used as a supporting electrolyte. Ge can be determined in the presence of a number of metals [126].

Titanium (IV) can be determined in a supporting electrolyte of sodium acetate in the presence of complexone III. Chromium and small amounts of iron do not interfere [118].

Uranium can be determined in the presence of Ni, Co, Zn, Mn, Al, Cr^{III}, Be and Tl in a supporting electrolyte of $(NH_4)_2CO_3$ and complexone III. Pb and Cu interfere [127].

Indirect polarographic methods based on the displacement principle, are also of great interest.

Calcium, for example, can be determined indirectly by using the wave which results from Zn^{2+} displacement from its complexonate with Trilon B. Ba is precipitated beforehand as $BaSO_4$. Only Mg^{2+} interferes [128]. Calcium has been determined in biological materials by this method [129].

Sulfates. SO_4^{2-} can also be determined indirectly by precipitating as $BaSO_4$, dissolving the latter in an ammonium solution of Ag-complexonate III and determining the Ag displaced polarographically. Ba can be determined in the same way [130].

The reduction potentials of many metals have been successfully separated by using complexone IV and others.

In the presence of complexone IV, it is possible, for example, to determine Cu and Bi in lead, thallium in bismuth, uranium in lead, etc. [131].

Amperometric Methods

Complexones possess a number of advantages as reagents for amperometric titration, since they form undissociated soluble complexes with most metals, and moreover have a high masking capacity which can be used during titration with other reagents. The examples given below illustrate these advantages.

Bismuth is very easily determined by direct amperometric titration with Trilon B, even in the presence of divalent cations, since it forms a stable complex at a pH at which the complexes of divalent cations are completely dissociated. Particularly valuable is the possibility of determining bismuth in the presence of any amounts of lead, and also in the presence of Zn, Cd, Cr, Al, As, Co and Mn.

Small amounts of Cu, Ag, Fe, Sb and Sn do not interfere.

Bismuth can be determined by this method in lead and its alloys [132].

Iron (III) can also be determined amperometrically with complexone III. Alkaline earth metals, tungstates, molybdates, manganese and the common anions do not interfere.

Nickel can be titrated in any media with pH 2-10 at 1.22-1.30 V. Tartrates and citrates interfere.

Lead should be titrated with complexone III in a solution with pH not less than 4 at 0.60-0.72 V. Nitrates, acetates, citrates, or tartrates can be used as supporting electrolyte.

Zinc + cadmium. Both cations are best titrated with complexone III in a weakly acid, neutral, or ammoniacal media at 1.2-1.45 V for Zn and 0.7-0.92 V for Cd [133].

Calcium. When Ca^{2+} is titrated with Trilon B, the diffusion current of Zn^{2+} is used as the indicator, since the latter will only react with Trilon B when all the Ca^{2+} has been complexed. Mg^{2+} does not interfere, if the concentration of the latter is not more than five times that of calcium [128].

The use of complexones as masking agents during amperometric titration with other reagents may be illustrated by the determination of thallium and silver.

Thallium can be determined amperometrically by titration with iodine in the presence of Pb, Bi, Cu and Fe, using complexone III in a solution buffered at pH 4 [134].

Small amounts of thallium can be determined in lead if it contains only small amounts of Cu, Fe and Bi [135].

Silver. In the presence of complexone III, many cations do not interfere with amperometric titration of silver with KI using a rotating platinum micro electrode [136].

Potentiometric Methods

Potentiometric methods have been widely used by Schwarzenbach and coworkers for studying the properties and structure of complexones and complexonates.

Potentiometric titration with complexones has a number of advantages as compared with titration with other complexing agents. Above all, they form stable and soluble complexes with di- and trivalent cations, and the rate of formation of these complexonates is very high. In addition, as a consequence of the fairly large difference in the instability constants of complexes of a cation in different valency states, new oxidation-reduction systems with a lower redox potential can be formed. For example, in the system Fe^{III}/Fe^{II}, the redox potential is +0.77 V, on addition of complexone III, the redox potential drops to +0.117 in the system FeY^-/FeY^{2-}; in the system Co^{III}/Co^{II}, the redox potential is + 1.79 V, while in the system CoY^-/CoY^{2-} it is + 0.6 V, etc..

Nevertheless, this condition is only fulfilled in a limited number of cases and as a result the method of potentiometric complexometric titration is of limited application, as can be seen from the examples given below.

Iron. The relation between potential and pH values has been studied for the system FeY^-/FeY^{2-} [137].

It is best to titrate Fe^{III} with a complexone at a pH of 3 using a platinum electrode as the indicator electrode. The potential jump at the equivalence point is equal to 200 mV, while at pH 5 it is 350 mV. F^- tartrate ions, Ca^{2+}, Ba^{2+}, Sr^{2+}, Mn^{2+} and UO_2^{2+} do not interfere with iron determination. Citrates and cations which form complexes with the reagent interfere [138].

Copper can be determined potentiometrically by titration with complexone III at 40-45°, after addition of NH_4CNS to the solution to set up the system Cu^{2+}/Cu^+. Mn^{2+}, Cr^{III}, As and Sb do not interfere.

Iron and copper can be determined when they are present together in solution. The first potential jump corresponds to Fe, while the second, after addition of NH_4CNS, corresponds to Cu.

Cu, Cd, Zn, Pb, Ni, Al. Each of these elements can be determined indirectly by titrating excess of added complexone III with a solution of $FeCl_3$ at a pH of 5-6. Nevertheless, as a consequence of the small differences in the values of the instability constants of the complexonates corresponding to these metals, they cannot be determined in mixtures with each other. Each of them on its own can be determined accurately even in the presence of Ca, Ba and Sr [139].

Bismuth can be determined indirectly, by titrating excess complexone III with $FeCl_3$ at pH 3-5. Cd, Zn, and Pb do not interfere as long as their amounts are not too large [138].

Iron and aluminum. When these two elements are present together in solution, their sum is first determined by titrating excess of added complexone with $FeCl_3$. Then, after addition of standard $FeCl_3$ solution, Al^{3+} is displaced from its complexonate according to the reaction

$$AlY^- + Fe^{3+} = FeY^- + Al^{3+}$$

and excess Fe^{III} determined potentiometrically. The aluminum content is calculated and the iron determined by difference. This method has proved a convenient one for the determination of Fe and Al after they have been separated during the ordinary course of analysis as hydroxides or acetates [139].

Masking by Complexones during Potentiometric Titration with other Reagents

As examples of masking by complexones we cite the titration of Mn, Co, Ag and U.

Manganese can be titrated with ferricyanide in the presence of Co, Fe, Ni, Cd, Zn, Cr, Al, Ti, Mo, W, Mg and the alkaline earth elements in ammoniacal solutions containing complexone III and KCN. Complexone III inhibits interference from Co, which as Co^{III} forms a very stable complex with Trilon B; complex MnY^- is unstable at elevated temperatures. To speed up oxidation of Mn^{2+} to Mn^{3+}, Ca^{2+} is added to displace Mn^{2+} from the complexonate according to the reaction

$$MnY^{2-} + Ca^{2+} = CaY^{2-} + Mn^{2+}.$$

Mn^{2+} forms a complex with $CN^- \rightarrow Mn(CN)_6^{4-}$, which is readily oxidized with ferricyanide. Fe^{III} is reduced to Fe^{II} by $Na_2S_2O_3$, but Cu and V^V must be removed.

Mn can be determined with great accuracy in ferromanganese in this way [140].

Manganese can also be determined by potentiometric titration with reducing agents in the presence of complexone III, in particular, by titration with Mohr's salt, if the MnY^{2-} is first oxidized to MnY^-.

Cu, Pb, Zn, Ni, Al, Cr do not interfere; W, Mo, Co and V do interfere, but W and Mo can be separated beforehand by precipitation with 8-hydroxyquinoline [141].

Silver can be determined potentiometrically with iodine in the presence of Pb, Cu, Bi, Cd, Fe, Ni, Zn and Tl, if complexone III is added [142].

Uranium can be determined indirectly by titration of NH_4 with $Ca(OCl)_2$. In this method, uranium is precipitated as ammonium diuranate or ammonium uranyl phosphate in the presence of complexone III, the precipitate is carefully washed free of excess NH_4^+ ions with ethanol; titration is then carried out in the presence of KBr after dissolving the precipitate in $NaHCO_3$.

Be and Tl do not interfere with titration of ammonium diuranate; V interferes; Be interferes during titration of the phosphate [143].

The Part played by Complexones in Creating New Redox Systems During Potentiometric Titration with Other Reagents

The capacity of complexones to lower redox potentials of systems can also be used for potentiometric oxidation-reduction titrations with other reagents, as is evident from the cerimetric titration of cobalt, and the oxidimetric titration of manganese, etc..

Cobalt. In the presence of complexone III, the redox potential of the system CoY^{-}/CoY^{3-} is equal to 0.6 V, so that Co^{2+} can be titrated with $Ce(SO_4)_2$.

Iron and many other cations do not interfere with the titration, Mn and Ni interfere. The method has been applied to the determination of cobalt in steel [144].

Cobalt can be determined by potentiometric titration of Co^{III} in the presence of complexone III, with Cr^{2+} salts. Mn, Ni, Zn, Al, Cr and small amounts of W do not interfere. Mo^{VI}, V^{V}, Fe^{III} and Cu^{2+} interfere [145].

Silver can also be titrated with reducing agents in the presence of complexone III; $FeSO_4$ in particular is used. Reduction is to the metal [146].

Complexones in Qualitative Analysis

Complexones have found wide application in macro- and microqualitative reactions as masking agents [147]. In their presence, several qualitative reactions become selective, for example, the reaction of Hg^{2+} and Ag^{+} with dithizone [73], Cu and Bi with diethyldithiocarbamate Cd as CdS, Sb^{III} as $HgSbCl_5$, etc..

Moreoever, complexone III itself gives characteristic colors with Cr^{III}, Co^{III} and Mn^{III}, which can be used for detection of these elements [70, 71, 72].

It is clear from this review which is by no means an exhaustive review of the literature on the properties and application of complexones, that the latter are exceptionally valuable compounds which have opened up new possibilities in the various branches of chemistry, in particular in analytical chemistry.

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DETERMINATION OF THE MAIN COMPONENTS OF CLAY, SPECTROGRAPHICALLY

E. E. Vainshtein, T. F. Borovik-Romanov and V. V. Korolev

The V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry

Academy of Sciences, USSR, Moscow

In order to solve a number of geochemical questions, it is essential that express methods of analysis be worked out for the analysis of the main components of silicate rocks. In particular, we came up against this necessity in work carried out in our Institute on Geochemical studies of clays of various orgins. A considerable amount of work has been done on the quantitative spectrographic determination of large amounts of the oxides of Si, Al, Cd, Fe, Mg and other elements in silicate minerals, ores, slags, ceramics, and some other materials. Mention may be made, for example, of the work of Korzh and coworkers [1-4], who used a spectrographic method for the quantitative analysis of iron and manganese ores and of basic manganese slags, that of Buyanov [5, 6], Veselovskaya [7], Aidarov [8], Matveev and Mikhailov [9], Rezvov and Kler [14], who determined the content of the main components of slags, cements, and clays; recently, the work of Nadezhdina [10], Danilova [11], Nalimov and Ionova [12, 13], and others has appeared. Of foreign research workers, mention may be made of the work of Kvalheim [17], Ashry and Schrenk [15], and Jaycox [16], Eeckhout [18], and others.

Two methods are possible for the spectrographic determination of large amounts of elements in a test sample. In the first of these methods the weak spectrum line of the element is used. In the second – determination is made by means of "final" lines, but the test sample is diluted 20-100 times. For this purpose, the sample is usually mixed in definite proportions with graphite powder and a buffer, which at the same time serves as a reference element. The buffer most often used is powdered metallic copper or the powdered metallic oxide. Sometimes, nickel oxide is used as a diluent and a reference standard [15], or a mixture of copper and nickel oxides [10], or a mixture of the carbonates of Sr and Be with quartz or NaCl [17]. Some authors recommend using PbO, Bi_2O_3 and $Ba(NO_3)_2$ for this purpose. Various methods of introducing the sample into the discharge zone have also been tried, burning the samples in a movable electrode, the method of complete evaporation in the crater of the arc anode, the briquetting method, and the "spilling" method. For excitation of the spectra, a condensed spark, and both A.C. and D.C. arcs have been used.

TABLE 1

Concentration limits of various components of clays (%)

SiO_2	Al_2O_3	MgO	Fe_2O_3	CaO
30.0-75.0	6.0-35.0	1.0-15.0	1.0-20.0	0.1-30.0

The aim of the present work was to develop a spectrographic method for the quantitative determination of the main components of clays, viz., the oxides of Si, Al, Mg, Fe, and Ca, the amounts of which in clays change within the limits indicated in Table 1. Bearing in mind the necessity of cutting down to a minimum the effect of "third components", the problem was solved by a dilution method. CuO* and carbon powder were used as the diluent and stabilizing bases. When the dilution method is employed, the accuracy of analysis depends on the purity of the copper oxide and carbon powder used; it is essential to check on the purity of these materials. It is desirable that the per cent contamination of the materials by the elements to be determined, should not exceed 0.001%. Selection of the optimum ratios of the components of the mixture was carried out experimentally by testing mixtures, in which the relative amounts of sample, copper oxide, and carbon powder were varied within wide limits from 1:10:80 to 1:60:40. We finally settled for the ratio 1:39:60 (10 mg sample + 0.39 g copper oxide + 0.8 g carbon powder).

Copper oxide was prepared from cupric nitrate by calcining the latter at 200-250°. In order to remove water adsorbed by the clay, the amount of which was sometimes considerable, the samples were given a preliminary drying at 105-110° for 1 hour. After this drying, the components were carefully mixed in an agate mortar for 20-30 minutes. The standard mixtures prepared as well as the samples were kept in containers fitted with ground glass stoppers. 30 mg of test sample was placed in the crater of the positive electrode of a D.C. arc. To prevent spattering, the sample was strewn with a small amount of carbon powder. The lower electrode had a depression 3.5 mm

* It was shown experimentally that the use of copper powder instead of the oxide led to less accurate results.

in diameter and 4 mm deep. The upper electrode was a spectrographically pure carbon rod, sharpened to the shape of a truncated cone with a diameter at the end of 2 mm. The spectra were excited with a D.C. arc operating at 10 A and 250 V.

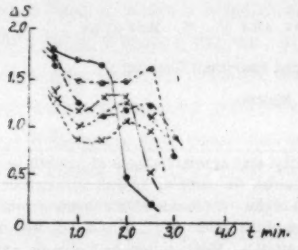

Fig. 1. Evaporation curves of the elements in clays.

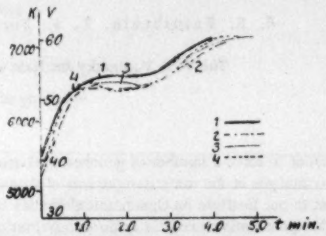

Fig. 2. Changes in arc flame temperature, and difference in potential V between the electrodes, respectively, during evaporation of various samples (1, 2, 3, 4) of clay (I= 10 A; l = 5 mm).

Using these conditions, evaporation curves were drawn for 4 samples containing varying amounts of the elements, and by measuring the potential difference between the tips of the carbon electrodes, the changes in temperature of the arc flame during the evaporation of the test samples were followed. Some of the curves obtained are shown as examples in Figs. 1 and 2. The shape of the evaporation curves is similar to the relation observed between arc flame temperature and time of evaporation. The curves in Fig. 2 relate to clay samples containing different amounts of the main components. In practice complete evaporation is achieved in $3\frac{1}{2}$ minutes. Regular passage of elements into the arc starts 10-15 seconds after starting the arc and continues for $1\text{-}1\frac{1}{2}$ minutes. An exposure time of 60 seconds was, therefore, selected.

The following lines were used for the respective elements:

Si – 2514.3A, Al – 3082.2A, Ca – 4226.7A and Ca – 3179.3A,

Mg – 2779.8A and Mg – 2802.7A; Fe – 2599.6A.

The three reference lines were

Cu – 4275.1A; 3073.8A and 2441.6A.

Results relating the lines chosen are given in Table 2.

TABLE 2

Element	Wave length (A)	Intensity arc	Intensity spark	Excitation potential (EV)
Si	2514.3	300	200	4.93
Cu	2441.6	200	100	5.08
Al	3082.2	800	800	4.02
Cu	3073.8	70	20	5.42
Ca	3179.3	100	400	7.05
Ca	4226.7	500	50	2.93
Cu	4275.1	80	30	7.74
Mg	2779.8	40	50	–
Mg	2802.7	150	300	4.42
Fe	2599.6	1000	–	5.68

TABLE 3

Standard No.	Chemical composition (%) SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
1	66.62	12.62	3.75	1.24	1.45
2	68.13	10.58	4.43	2.88	2.71
3	43.38	15.65	6.19	8.9	7.06
4	49.2	32.5	1.86	0.18	1.02
5	32.88	8.46	3.44	14.94	11.1
6	30.27	7.95	4.13	25.4	4.05
7	48.86	31.53	1.43	1.4	0.5
8	40.13	12.3	21.7	0.19	3.8

Different lines were used according to the concentration of MgO and CaO in the samples. In clays where the MgO content varied from 0.5 to 2% and CaO from 0.5 to 1%, the analytical lines used were Mg – 2802.7A and Ca – 4226.7 A. In samples were the MgO and CaO contents were higher, determination was carried out by means of the lines Mg – 2779.8 A and Ca – 3179.3 A.

The central part of the arc was projected by means of a triple lens condenser, through an intermediate diaphragm 5 on to the slit of a spectrograph Q-24. Spectra were recorded on "diapositive" plates with sensitivity 0.5 GOST. In a series of special tests, the extent of the "homologousness" of the selected pairs of test element lines and reference element was checked.

In constructing calibration curves, samples of clay whose composition has been determined by classical chemical methods were used as standards. The chemical composition of the standard clay samples is given in Table 3.

By means of this group of standards, which were registered on the same plate as the test clay samples, calibration curves were drawn in the coordinates ΔS and log C. A typical series of graphs for 5 of the test elements is represented in Fig. 3.

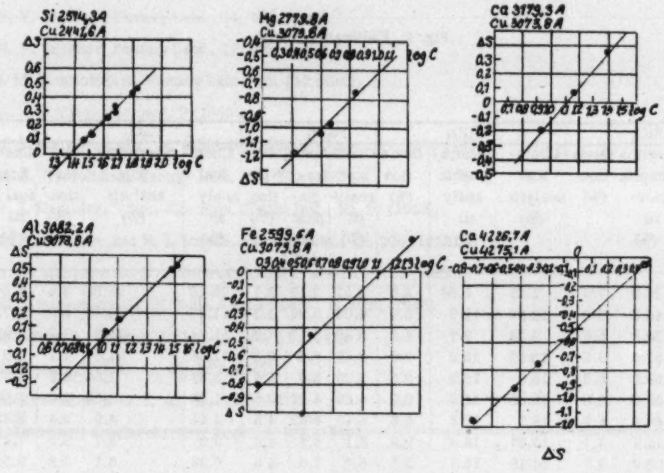

Fig. 3. Calibration curves.

It is clear that the calibration curves are straight lines in the concentration range we are interested in. In order to check the reproducibility of the method of analysis described, results of determinations carried out in parallel on the contents of Al, Fe, Ca, Si, and Mg were compared. The mean arithmetic error in 8 parallel determinations of these elements varies within the limits 1.5 to 6%.

Al_2O_3 – 1.4%; Fe_2O_3 – 2.5%; CaO – 4.3%;

SiO_2 – 4.5% and MgO – 5.8%.

The effect of test elements on one another was checked in a special series of experiments. To do this each of the five elements were added in turn, in known amounts, and in the same form in which they are normally present in clay, into a test. Subsequently, the behavior of the calibration curves for all the other elements was studied, for a group of samples differing considerably from each other in their contents of the components. As shown experimentally, the calibration curves remain unchanged, while the points corresponding to samples diluted with one of the components, lie on the same graph at locations in exact agreement with calculation. What has been said is illustrated by the graphs of Fig. 4. Here the various ciphers denote points relating to samples of clay, with widely differing Mg contents.

* Chemical analysis of standards and samples of clay was carried out by the Geochemistry Laboratory of our Institute.

Similar results which point to the absence of any mutual effects of the elements on one another, were obtained for all the test components of the clays.

The method developed was first used to analyze 35 samples of clay of varying geological ages, the elemental composition of which was determined in parallel chemically.

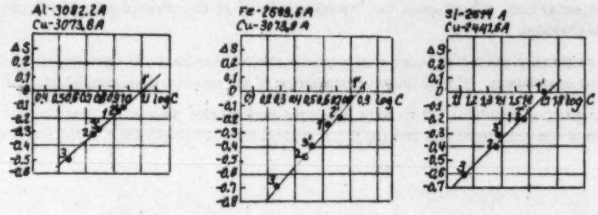

Fig. 4. Calibration curves

TABLE 4

Sample No.	SiO_2			Al_2O_3			Fe_2O_3			CaO			MgO		
	Chemical analysis (%)	Spectrographic analysis (%)	Deviation (%)	Chemical analysis (%)	Spectrographic analysis (%)	Deviation (%)	Chemical analysis (%)	Spectrographic analysis(%)	Deviation (%)	Chemical analysis (%)	Spectrographic analysis (%)	Deviation (%)	Chemical analysis (%)	Spectrographic analysis (%)	Deviation (%)
1	27.96	26.0	7.0	5.69	5.86	3.0	3.21	3.10	3.1	25.15	26.2	4.0	8.5	9.1	7.0
2	45.92	46.8	2.0	12.12	12.8	6.0	5.98	5.90	1.3	11.07	10.1	9.0	6.73	6.6	1.5
3	36.14	38.5	6.6	9.33	9.7	4.3	3.88	4.17	7.0	11.74	11.9	1.7	1.92	1.91	0.5
4	47.8	51.0	6.2	13.12	13.2	0.8	6.62	6.8	0.3	11.66	11.8	1.1	3.9	4.17	5.1
5	63.1	59.8	5.3	15.8	16.2	2.5	5.29	5.6	5.6	1.87	1.64	10.5	1.97	1.88	5.1
6	63.56	59.6	6.3	15.33	15.9	3.9	4.69	4.07	13.0	1.69	1.66	1.8	1.68	1.75	6.0
7	53.2	54.4	4.2	18.7	17.8	5.3	4.42	4.62	4.5	4.11	4.0	2.4	3.83	3.93	2.7
8	47.9	44.7	6.7	15.07	16.5	9.3	6.1	5.7	6.5	9.2	9.7	5.5	7.27	7.35	1.1
9	52.28	53.0	0.6	14.19	14.7	3.5	6.7	7.0	4.5	6.08	6.1	0.3	2.59	2.48	3.9
10	50.0	49.2	1.6	13.0	13.3	2.3	7.3	6.7	8.2	7.24	6.85	4.2	5.58	—	—
11	30.31	30.9	2.0	7.74	8.2	5.1	4.19	4.29	2.4	24.93	24.5	1.6	3.7	3.95	8.1
12	63.03	62.6	0.6	16.09	15.2	5.6	7.84	7.95	1.3	0.06	>0.5	—	1.68	1.84	6.0
13	62.8	64.6	2.9	16.36	16.8	2.4	7.89	8.0	1.3	0.05	>0.5	—	1.85	1.84	0.5
14	68.1	68.5	0.6	15.02	14.6	2.7	6.23	6.8	8.0	0.06	>0.5	—	1.29	1.18	8.5
15	40.1	41.5	3.5	11.48	11.4	0.7	4.72	4.82	2.1	20.15	20.0	0.8	1.92	2.0	4.1

An idea of the degree of agreement beween results of spectrographic and chemical analysis can be obtained from a consideration of the results given in Table 4. Each figure relating to spectrographic results is the mean of six independent determinations on two plates. The mean deviation of the spectrographic results from those of chemical analysis is slightly different for each element and varies in round numbers, within the limits 4-8%.

SUMMARY

1. A spectrographic method is described for the quantitative determination of the main components of clay, viz., the oxides of Si, Al, Fe, Mg and Ca. The reproducibility of a determination for the various elements are Al_2O_3 – 1.4%, Fe_2O_3 – 2.5%, CaO – 4.3%, SiO_2 – 4.5%, MgO – 5.8%. The mean deviation from the results of chemical analysis is 4-8%.

2. The method was tested on samples of clay of differing geologicalage, containing SiO_2 in the concentration range 30-75%, Al_2O_3 from 6 to 35%; Mg from 1 to 15%, Fe_2O_3 from 1 to 20%, and CaO from 0.1 to 30%.

3. On observing the experimental conditions we used, it was shown that the elements do not affect one another.

4. The technique employed may be applied without essential modifications to the quantitative determination of the same elements in other silicate rocks, in particular, granitoids.

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LITERATURE CITED

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A MICRO METHOD FOR THE DETERMINATION OF PRIMARY AROMATIC AMINES BY POTENTIOMETRIC TITRATION WITH SODIUM NITRITE

L. M. Litvenenko and A. P. Grekov

The A. M. Gorky Kharkov State University

The method most widely used for the quantitative determination of aromatic amines is diazometric titration of a strong mineral acid solution of the amine with sodium nitrite. This method is based on the following reaction:

$$ArNH_2 \cdot HCl + NaNO_2 + HCl \rightarrow ArN_2Cl + 2H_2O + NaCl.$$

The appearance of free nitrous acid at the equivalence point is fixed by means of starch-iodide paper. This method, which is generally accepted at the moment, apart from errors connected with the use of an external indicator, has a number of disadvantages: as a result of insufficient sensitivity of starch-iodide paper to nitrous acid, particularly in dilute solution [1], and its tendency to acquire a blue color in strong acid solution [2, 3], similar to the blue color to which nitrous acid gives rise, the equivalence point is often not clearly defined; titration has usually to be carried out in the cold (0-5°), and cases where titration can be effected at higher temperatures are limited; toward the end point it is necessary to keep the solutions for some time, before adding fresh amounts of titrant, in order to make sure of complete diazotization, the time of completion of which depends on the reactivity of the given amine. When this method is used, it is best to use large amounts of amine (ca. 1 g), and in certain instances to carry out preliminary orienting tests, so as to select optimal conditions for carrying out a given determination and finding out requisite precautions to be taken [2-5]. This method is not suitable for the analysis of colored solutions.

In 1925, the possibility was demonstrated of determining aromatic amines by potentiometric titration [6]. This method is based on the fact that the appearance of free nitrous acid at the end of diazotization is accompanied by a potential jump on a platinum electrode. Subsequently, some more work was published [7-10], as a result of which it became clear that the electrometric method has a number of advantages over titration controlled with starch-iodide paper.

A platinum indicator electrode indicates the end point more clearly and fixes it more accurately than starch-iodide paper, and even a large excess of mineral acid is no cause for worry. The potentiometric method does not require cooling of the liquid being titrated, so that titration is speeded up. It has been shown that heating even to 80° [7] has no ill effects; on the contrary, it favors an even sharper potential change. When an electrometric method is used there is no need for any preliminary tests, since the path taken by a reaction can be followed via potential changes with time, up to the point where the potential becomes a constant. When one remembers that the potentiometric method allows determination of aromatic amines to be carried out in non-aqueous media, and also in intensely colored solutions, then its advantages over the external starch-iodide indicator are obvious. All the same, despite these advantages, electrometric determinations of aromatic amines have still not been used to the extent they should be in organic analysis.

The positive aspects of the potentiometric method are so considerable that they give rise to the hope that it can be used, after some development, for the determination of micro amounts of amines. Taking into account the fact that 1 mole of amine combines on diazotization with 1 mole of nitrite, then on switching from the macro to the micro scale, it should be convenient to use a 0.01 N solution of nitrite and use a micro instead of an ordinary buret. Using a solution of this strength, 1-5 ml of nitrite should titrate 0.01-0.05 mM of amine. It is essential, however, to bear in mind the comparatively slow rate of diazotization, which renders the use of dilute nitrite solutions difficult during diazometric titration. It has been pointed out [10], for example, that the potentiometric method gives inaccurate results at nitrite concentrations of less than 0.5 N in a number of cases.

EXPERIMENTAL

Sulfanilic acid, aniline, p-nitroaniline, m-nitroaniline, 4-aminodiphenyl, 4-amino-4-nitro-2,2'-dichlorodiphenyl, and benzidine, were systematically studied. The solid amines were purified by recrystallization until

constant melting points were obtained; aniline was distilled a few times over zinc dust, while sulfanilic acid was purified by a method used for preparing the analytically pure product [2, 3]. All the amines were dissolved in dilute hydrochloric acid of a definite concentration to give exactly 0.01 N solutions, 5 ml of these solutions was taken for analysis (2.5 ml in the case of benzidine).

A P-4 potentiometer from the MOSKIP factory was used for measuring E.M.F. A galvanometer with a sensitivity of $1.5 \cdot 10^{-7}$ A per scale division and with a resistance of 305Ω was used as null point instrument. A plate platinum electrode such as described in the papers cited above was used. The auxiliary electrode was a quinhydrone electrode (prepared fresh weekly), the standard solution for which was a Webel buffer mixture (0.01 N HCl + 0.09 N KCl). All experiments were carried out at room temperature. 0.01 N sodium nitrite was used as titrant; this solution was standardized potentiometrically with sulfanilic acid in the presence of potassium bromide (see below). Nitrite solution was kept in a flask protected from the atmosphere by a flask filled with an alkaline pyrogallol solution. Such a set-up ensured good stability of the nitrite solution for at least 2 months. Titration was carried out from a 10 ml buret with scale divisions of 0.2 ml, and having a tip ca. 60 mm long and an internal diameter of 0.5 mm. Under these conditions, loss of sodium nitrite when the tip of the buret was introduced into the liquor being titrated, as a result of diffusion was negligible and in practice did not lead to errors. At the start of a titration, nitrite solution was added in 1-2 ml lots, but toward the equivalence point, it was added in 0.02 ml lots.*

TABLE 1

Examples of Some Determinations (amount of amines, 0.05 mM; V, volume of 0.01 N nitrite solution in ml; E, potential difference in millivolts)

Sulfanilic acid			Aniline			n-Nitroaniline		
V	E	$\frac{\Delta E}{\Delta V}$	V	E	$\frac{\Delta E}{\Delta V}$	V	E	$\frac{\Delta E}{\Delta V}$
0	99	–	0	125	–	0	196	–
2	124	12.5	2	170	22.5	2	201	2.5
4	140	8	4	190	10	4	212	5.5
4.92	182	45.6	4.92	222	35	4.92	290	85
4.94	196	700	4.94	229	350	4.94	296	300
4.96	225	1450	4.96	238	450	4.96	306	500
4.98	256	1550	4.98	255	850	4.98	336	1500*
5.00	298	2100*	5.00	290	1750*	5.00	346	500
5.02	318	1000	5.02	305	750	5.02	354	400
5.04	326	400	5.04	315	500	5.04	358	200
5.06	329	150	5.06	320	250	5.06	364	300
5.08	331	100	5.08	324	200	5.08	367	150
			5.10	326	100	5.10	369	100

* Equivalence point.

Preliminary tests showed that at such dilutions, the potential is established very slowly. This complicated work considerably and did not lead to accurate results. However, on adding potassium bromide to the solution being titrated to serve as a catalyst [2, 4], the position was radically improved. Thus, for a concentration of potassium bromide in the solution being titrated of from 0.3-0.4 N, the potential after addition of 0.02 mole nitrite near the equivalence point (when the reaction slows down appreciably) in the case of such slightly basic amines as the nitroanilines or sulfanilic acid, became constant after a few seconds; during determination of more basic amines (aniline, 4-aminodiphenyl) the potential took 1-3 minutes to establish itself. Further increases in KBr concentration did not essentially affect the rate of diazotization.** Consequently, in further tests, we stuck to the concentration indicated above for KBr.

It is of interest to note that in the first moment after addition of each aliquot of nitrite, the potential momentarily increases (this is probably determined by the presence in the mixture of a large number of NO_2^- ions), it then gradually falls to a definite constant value, which is the one recorded.

* It is easy to judge when one is approaching the end point, since the potential jump for all the amines tested on the set-up we used was observed within almost the same E.M.F. range.

** In previous work on potentiometric titration of amines, the catalytic action of KBr was not used; this probably explains why comparatively high concentrations of nitrite were used in these cases.

In order to clarify the effect of mineral acid concentration on the titration process, tests were carried out with 0.01 N amine solution in 2, 10, and 20% hydrochloric acid. It was shown that changes in acid concentration do not appreciably affect the accuracy of determination. In subsequent experiments, therefore, the amines were titrated in 10% acid.

Since on examining a greater number of test amines one often comes up against amines whose hydrochlorides are sparingly soluble in aqueous solutions, we studied the effect of acetic and formic acid in the solution being titrated. It was found that amines dissolved in 10% HCl containing from 10-80% of acetic or formic acid can be titrated in exactly the same way as purely hydrochloric acid solutions of the amines. For example, we determined benzidine and 4-aminodiphenyl in a 10% HCl solution prepared from 50% acetic acid, and 4-amino-4'-nitro-2,2'-dichlorodiphenyl in a similar formic acid solution. The potential jump for the titration of benzidine occurs at the point corresponding to complete diazotization of both amino groups.

Some of the results on amine determinations carried out under the conditions described are adduced in Table 1.

The accuracy of the results obtained was evaluated by means of the formula [11]:

$$\bar{x} = \bar{x} \pm t_{\alpha} S_x,$$

where $\bar{x}$ is the mean value of the results of n determinations for each amine, t_{α} is a factor depending on the number of determinations n for a confidence level of 0.95; $S_{\bar{x}}$ is the mean square error of the mean value calculated according to the formula:

$$S_{\bar{x}} = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n(n-1)}},$$

where x_i is the result of a separate determination. The results obtained are collected in Table 2.

TABLE 2

Accuracy of Determination of Amines

Amine	n	Found (%)
Sulfanilic acid	8	100.0 ± 0.1
Aniline	5	100.0 ± 0.9
m-Nitroaniline	5	100 ± 1
p-Nitroaniline	5	99.2 ± 0.1
4-Aminodiphenyl	5	99.3 ± 0.4
4-Amino-4'-nitro-2,2'-dichlorodiphenyl	4	99.8 ± 0.4
Benzidine	5	99.4 ± 0.6

The micro method described above for the determination of aromatic amines has been successfully used for a year in the scientific research laboratories of the Organic Chemistry Section of Kharkov University. ca. 100 aromatic amines with the most varied structures have been determined by this method. In the course of this work, we came across amines whose hydrochlorides were insoluble in acetic acid and in formic acid solutions (e.g., some aminophenylimides of naphthalic acid). In some of these cases, determinations were carried out by resorting to a technique proposed by E. E. Khotinskaya.

The amines were dissolved in hot concentrated sulfuric acid, which was then diluted with glacial acetic acid and analysis carried out as usual.

In some cases we managed to carry out successful determinations of amines in amounts of 0.003 mM. This indicates that, if necessary, it should be possible, by decreasing the concentration of nitrite and increasing the sensitivity of the galvanometer, to develop our method for determining even smaller amounts of amines.

The use of the catalytic effect of KBr should also be beneficial in the macro variant of this method (using a 50 ml buret and 0.1-0.2 N nitrite solution).

Recommended Analytical Procedure

An aliquot of the amine (0.01-0.05 mM) is dissolved in 5-20 ml of 2-10% hydrochloric acid. If the amine is sparingly soluble in water, then it might be necessary to dissolve it in acetic or formic acid and add concentrated hydrochloric acid until the HCl concentration of the final mixture is ca. 2-10%.* KBr is then added in sufficient amount to give a concentration of not less than 0.3-0.4 N.

* It follows from what was said earlier than where necessary it is not essential to hold precisely to this concentration of HCl.

The liquid to be titrated is stirred vigorously with a mechanical glass stirrer, and the 0.01 N sodium nitrite added from a buret, the tip of which is immersed in the liquid, nitrite is added first in fairly appreciable amounts, and then in smaller amounts as titration proceeds, until, when the equivalence point is near, titrant is added in 0.02 ml amounts. The equivalence point is fixed by the maximum increase in potential $\frac{\Delta E}{\Delta V}$.

Calculation is carried out according to the following formula:

$$\% \text{ amine} = \frac{a \cdot T \cdot 100}{b},$$

where a is the number of mls of nitrite used in the titration; T is the standard titer of nitrite with respect to amine; b is the weight of amine taken.

SUMMARY

1. A micro method has been developed for determination of primary aromatic amines by potentiometric titration with sodium nitrite.

2. It has been shown that aromatic primary amines with the most diverse structures and basicity can be determined by this method equally well, with an accuracy of up to 1% and within a wide pH range, by using the catalytic action of potassium bromide.

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ACIDIMETRIC DETERMINATION OF PHENOLS

E. T. Lippmaa*

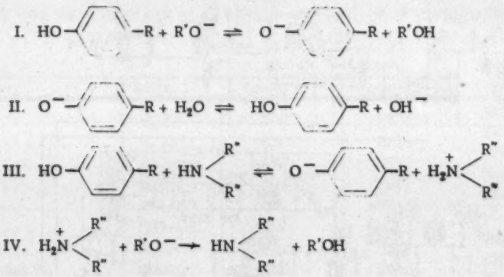
Tallin Polytechnic Institute

The determination of phenols is of considerable importance in the analysis of mineral oils, in particular in tar obtained from thermal treatment of solid fuel. Determination of the amount of phenol hydroxyl groups is of essential significance in establishing the structure of unknown organic materials. Total phenols are normally determined by extraction with aqueous or alcoholic alkali. Kunin, Melnikova, and Lagutkina have suggested a refractometric method for determining phenols in tar from semi-coking [1]. A colorimetric method has also been suggested for phenol determination [2]. These methods, however, are not universally employed. Many phenols, particularly highly alkylated phenols, do not react with aqueous alkali.

The use of metalo-organic compounds or organic acid anhydrides very often serves as the basis of methods for determination of phenol hydroxyl groups. Nevertheless, metallo-organic compounds do not react quantitatively with monohydric phenols [3]. Acetylation in pyridine solution gives considerably better results [4]. These methods do not permit distinction between phenol hydroxyl and alcohol hydroxyl groups.

Direct titration of phenol hydroxyl groups in aqueous solution is impossible. Moss, Elliott, and Hall titrated phenols and carboxylic acids with sodium aminoethoxide in ethylenediamine solution [5]. Katz and Glenn adopted their method for titrating highly alkylated phenols [6]. Nevertheless, hydroquinone, phloroglucinol, and 2,6-diamyl-p-cresol reacted to only 60% of theory. Fritz and Keen successfully titrated monohydric phenols and carboxylic acids with potassium methylate in a solution of ethylenediamine and dimethylformamide [7]. Their method proved unsatisfactory for polyhydric phenols.

The author of this paper holds the view that direct titration of phenols can be carried out succesfully only in strongly basic solvents. When phenols are titrated with the alcoholates of the alkali metals, the following reactions may occur:



When titration is carried out in aprotic solvents the reaction follows scheme (I). In strongly basic solvents, reaction (III) occurs, and all compounds having acid properties form $H_2\overset{+}{N}\begin{matrix}HR''\\R''\end{matrix}$ ions. As a result of this, the solvent evens out the strengths of the various acids and imparts clearly defined acid properties even to phenols. During titration, neutralization occurs according to scheme (IV) with a clear cut equivalence point. The "amphiprotic" properties of the solvent are detrimental, since they favor reaction (II) and make titration impossible. For this reason, the solvent should be free from water and appreciable amounts of alcohol.

* Under the direction of A. Ya. Aarna.

Determination of the equivalence point can be carried out in the presence of indicators, potentiometrically, or conductometrically. In the case of colored solution, the last two methods have obvious advantages. Potentiometric or conductometric titration can be successfully carried out in solvents with a dielectric constant of not less than 12-16. In our case, we applied a H.F. conductometric method. H.F. (high frequency) titration has one important advantage over other electrometric methods, viz., the absence of internal electrodes, the potentials of which do not get to a steady equilibrium state in basic solvents.

EXPERIMENTAL

A mixture of the following composition was used as solvent: 450 ml diethylamine (technical grade, containing roughly 30% triethylamine), 350 ml diethylformamide; 200 ml of pyridine and 1 g thymol.

A 0.2 N solution of potassium methylate of the following composition was used as titrant: 840 ml pyridine, 60 ml benzene, 108 ml methyl alcohol, and 13 g of metallic potassium.

All the components were carefully dehydrated. Diethylamine, diethylformamide, and pyridine were dried by working them up with KOH and then distilling them at atmospheric pressure. Diethylformamide was synthesized from diethylamine and formic acid [9]. The fraction boiling between 175-180° was chosen.

The methylate solution was prepared by dissolving metallic potassium in a mixture of methyl alcohol and benzene and then diluting with pyridine to 1 liter.

From what has been said above it follows that the solvent used for conductometric titration (including H.F. titration) should have clearly defined properties: a sufficiently high dielectric constant, it should be as basic as possible, and it should readily dissolve the starting materials and reaction products (phenols, alcoholates, and phenolates). Unfortunately, there is no single substance known at present which satisfies all these requirements at the same time. We decided to use strongly basic diethylamine to which diethylformamide was added to increase the dielectric constant, and pyridine to improve its solvent properties. Addition of thymol improves the equivalence point during titration of carboxylic acids and some polyhydric phenols. Thymol itself gives a very good equivalence point, which is reached just after those of the carboxylic acids, so that it can be used for "developing" the equivalence points of the latter.

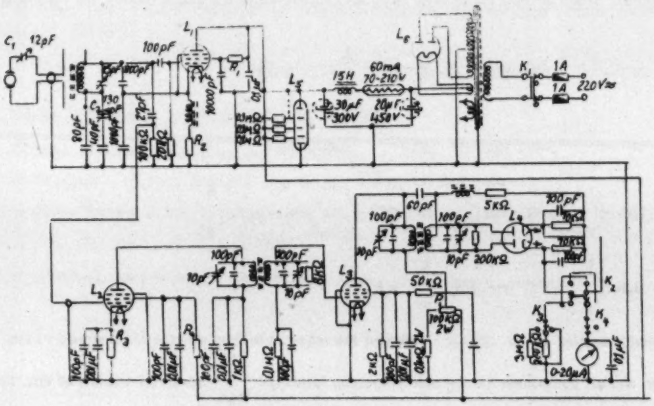


Fig 1. Scheme of the H.F. titration set-up.

A large number of solvents were tried. Pure diethylamine was found to be unsuitable on account of its low electrical conductivity. On carrying out titration in a mixture of diethylamine with various alcohols, equivalence points were only obtained for carboxylic acids. Ethylenediamine is a poor solvent for mineral oils and no equivalence points were obtained in carrying out H.F. titration of phenols in it. Poorly defined equivalence points were also

obtained in pure diethylformamide and pyridine. Diethylamine and diethylformamide (1:1) may find limited application. This solution is well-suited for titration of monohydric phenols; nevertheless, benzoic acid and polyhydric phenols do not give satisfactory results. There is also an optimum composition for the titrant; 0.15 N solutions of potassium and sodium alcoholates in benzene, pyridine, diethylamine and in its mixture with diethylformamide (1:1), proved unstable and in some cases gave unsatisfactory equivalence points. It was shown in the course of the present investigation that the best equivalence points were obtained when the alcohol concentration is a minimum. Pyridine readily dissolves alcoholates, and the solution of potassium methylate in pyridine-methanol is better than the solution in benzene-methanol suggested by Fritz [7].

It is particularly important to protect the solution from atmospheric carbon dioxide and moisture. The flasks containing the solution were, therefore, provided with calcium chloride tubes partly filled with ascarite.

Equivalence points were determined by means of a H.F. apparatus operating at a frequency of 3.6 Mc. The set-up is shown schematically in Fig. 1

The titration cell (Type "C" [10]) is connected via a variable condenser with the H.F. generator circuit (L1). The generator operates on a capacitative feed back. Such a generator is very stable, since the relatively large condensers of the circuit are connected in parallel to the tube electrodes, and the coupling between tube and circuit is very loose. The H.F. current from the generator is amplified in an intermediate amplifier L2 to the tube required for operating limiter L3. The H.F. transformer preceding L3 should have a wide band width. The output voltage after limiter L3 is practically independent of the voltage in front of it. From limiter L3 the H.F. current with constant amplitude proceeds into the frequency detector L4. A constant voltage is developed between the cathode of the detector, the value and polarity of which depend on the difference between the frequency of the incoming H.F. current and the characteristic detector frequency. The output voltage of the frequency detector is measured with a sensitive microammeter. Since the limiter "cuts off" all the vibrations of the H.F. current voltage supplied by the generator, this apparatus is a pure "F-meter" [10]. It is easier to use than other F-meters, since frequency measurements are carried out directly without compensation.

The variable condenser C_2 is used for building up the frequency of the generator before starting to titrate and if necessary during titration. Potentiometer P_1 and throw-over switch K_3 allow the sensitivity of the apparatus to be changed. During titration, the maximum sensitivity is used while between titrations minimum sensitivity is used. Intermediate sensitivity is necessary for coarse adjustment of the microammeter needle to zero before titration (by building up the frequency). The anode potential of the apparatus is stabilized. The time to warm up after switching on is 20 minutes. Maximum drift is 0.05 μ A/minute.

Different line ups of tubes can be used in the set-up, if minor modifications indicated in Table 1 are made.

TABLE 1

Component	Series I	Series II	Series III
L1	6Zh4	6AC7	EF14*
L2	6Zh4	6AC7	EF14
L3	6Zh8	6Sl7	EF12
L4	6Kh6	6H6	EB11
L5	SG-227	—	STV280/80
L6	VO-188	80	AZ1
Anode voltage	280V	280V	210V
Resistance R_1 and R_4	65KΩ	5KΩ	200Ω
R_2	50Ω	50Ω	200Ω
R_3	160Ω	160Ω	330Ω

* The original set-up was made with Series E tubes.

The cell used for titration is shown in Fig. 2. It is made from chemically stable glass. Annular copper electrodes are fitted on its lower end; these are connected with a H.F. two-wire cable. The screen of the cable is connected to the cell screen. The glass underneath the copper electrodes is platinized for greater stability. The value of the connecting condenser is critical. If this capacity is too high, the shape of the titration curve is distorted and the generator may even stop working. If the capacity is too low, the sensitivity drops.

10-100 mg of sample containing ca. 0.0003 g-equivalents of acid hydroxyl was used for titration. Exactly 25.00 ml of solvent was measured into the cell from a buret followed by 0.1 ml of potassium methylate solution. After addition of each portion of solvent, the frequency of the generator was measured on the microammeter in arbitrary units. The equivalence point is characterized by the last sharp change in the rate of frequency change. Fig. 3, contains 7 typical titration curves.

Titration of monohydric phenols and phenol containing tars takes ca. 20-50 minutes, unsubstituted monohydric phenols — up to 4 hours. Results of titration are given in Table 2.

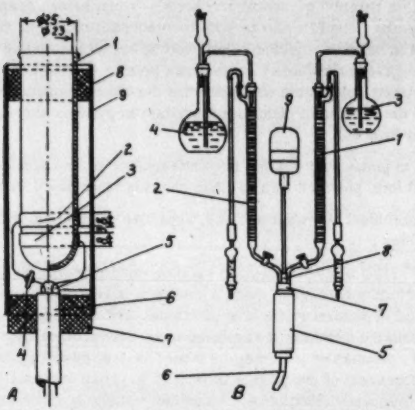


Fig. 2. A) Titration cell. 1) Glass cell; 2, 3) copper electrodes; 4) condenser C_1: 5) polystyrene insulator; 6) high frequency cable; 7, 8) rubber stoppers; 9) screen. B) Titration apparatus. 1) Buret for titrant (10 ml); 2) buret for solvent (50 ml); 3, 4) bottles; 5) titration cell; 6) high frequency cable; 7) rubber stopper; 8) rubber seal for stirrer; 9) stirrer.

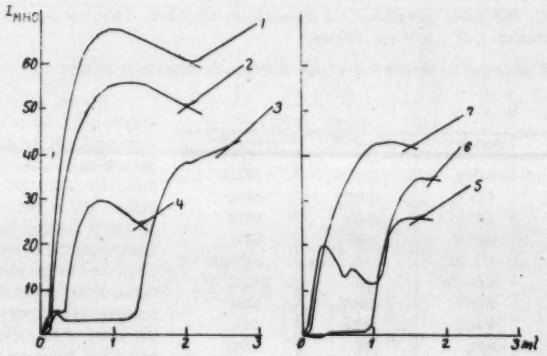


Fig. 3. 1) p-Butylphenol; 2) β-naphthol; 3) pyrogallol; 4) 2,4-dimethylresorcinol; 5) resorcinol; 6-pelargonic acid; 7) shale tar.

As the results show, the method suggested is applicable to the titration of phenols, enols, and carboxylic acids. Of the hydroxy alcohols, only glycols are titrated. The method is not suitable for titrating strong acids. Acids below caproic acid form precipitates and give poorly defined end points. Benzoic acid is titrated with difficulty. Dihydric phenols give the greatest deviations from theory, possibly because of the formation of a precipitate at the beginning of titration. Precipitate formation hinders the normal course of the reaction and titration is slowed up considerably. Titration rate increases with the extent of the substitution of the phenols. Thus, 2,4-dimethylresorcinol is titrated 4 times faster than resorcinol and with ca. half the error.

TABLE 2

Compound	Number of acid hydroxyl groups		Compound	Number of acid hydroxyl groups	
	theoretical	found by titration		theoretical	found by titration
					0.997
Phenol	1	0.989	Morphine + HCl + $3H_2O$	1	1.99
o-Cresol	1	1.005			together
o-Phenylphenol	1	1.004			with HCl
p-Phenylphenol	1	1.009	Pelargonic acid	1	1.036
Thymol	1	1.000	Benzoic acid	1	1.008
p-Butylphenol	1	1.011	Caproic acid	1	1.050
α-Naphthol	1	1.002	Acetoacetic ester	1	1.015
β-Naphthol	1	0.975	Benzyl alcohol	–	0
Hydroquinone	2	1.93	Triphenylcarbinol	–	0
2,5-Dimethylhydroquinone	2	1.91	Octanol-2	–	0.015
Resorcinol	2	1.73	Chloesterol	–	0
2,4-Dimethylresorcinol	2	1.85	1-Pentenol-4	–	0
Pyrocatechol	2	2.21	Ethyleneglycol	–	0.69
Pyrogallol	3	3.15	Benzophenone	–	0
Phloroglucinol + $2H_2O$	3	3.15	Methylethylketone	–	0
8-Hydroxyquinoline	1	0.949	Benzaldehyde	–	0

The method gives reproducible results (in duplicates, the deviation from the mean is not greater than ± 1%).

The method can be successfully applied to the titration of mineral oils. Even high-boiling fractions from shale tar give good equivalence points. It was established that shale tar from which phenols have been removed still contains a considerable amount of acid hydroxyl groups. Table 3 contains some results on titration of shale tar.

TABLE 3

Fraction	Hydroxyl group content (in %)	
	by titration	by acetylation in pyridine
Shale tar fraction 100-225°/2 mm Hg	6.09	5.51
Shale tar fraction 100-225°/2 mm Hg after removal of phenols with 10% NaOH	1.49	1.37

SUMMARY

1. A method has been developed for the titration of acid hydroxyl groups in basic solvents.

2. It has been shown that phenols, enols, and carboxylic acids can be titrated in basic solvents. This method gives best results with monohydric phenols. Alcoholic hydroxyl groups are not titrated except those of glycol. That the method can be used, has been shown by titration of various individual compounds.

3. A high-frequency set-up has been designed and constructed for high-frequency titration in basic solvents.

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POLAROGRAPHIC DETERMINATION OF SACCHARIN

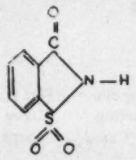
M. B. Neiman

Institute of Chemical Physics, Academy of Sciences USSR, Moscow

Quantitative determination of saccharin in complex mixtures is very difficult. Meyer suggested determining saccharin by titration [1], but the method is impracticable in the presence of colored materials, and other acids, or if the saccharin is present as the sodium salt. The colorimetric methods of Rozanov [2], and Soifer [3], have also very limited application.

In 1934, Pech showed that saccharin in acid, neutral, or alkaline solution is reduced on the dropping mercury cathode and used a polarographic method for determining saccharin in tablets [4].

The saccharin molecule



contains the group C=C−C=O, the electrical reduction of which on the dropping mercury cathode is characterized by some peculiarities noted in a number of papers devoted to polarographic determination of unsaturated aldehydes and ketones [5-7].

All these compounds exist in two forms, one of which is stable in acid, and the other in alkaline solutions.

In the present investigation, we studied the electrical reduction of saccharin in acid, alkaline, and neutral solutions and on the basis of this work we have proposed a polarographic method for the determination of saccharin in syrups.

We used a visual type polarograph from the Gorky Institute of Chemistry and used two capillaries with the following characteristics: 1.67 $mg^{2/3}$ $sec^{-1/2}$ (A) and 1.41 $mg^{2/3}$ $sec^{-1/2}$ (B).

The first tests showed that the caracter of the polarographic waves obtained for solutions of $5 \cdot 10^{-3}$ mole/liter of saccharin is strongly dependent on the pH of the supporting electrolyte.

In 0.1 N HCl the wave starts at −1.2 V and $E_{1/2}$ = −1.24 V with respect to the normal calomel electrode. In 0.1 N NaOH the wave starts at ca. −1.6 V while $E_{1/2} \cong$ −1.78 V. In both cases $I_{diffusion} \cong$ 50 μA.

In 0.1 N LiCl reduction occurs in two steps, each of approximately the same height, the half wave-potentials of the two steps are respectively, −1.96 and −2.22 V.*

The type of curves obtained with the different supporting electrolytes is shown in Fig. 1 when capillary B was used.

Pech [4], also took polarograms of saccharin in acid and neutral solution, but did not pay attention to the fact that the diffusion current in the first instance is double that in the second.

In acid solutions, saccharin undergoes some changes on standing, probably as result of hydrolysis, which can be followed polarographically. In a solution of $5 \cdot 10^{-3}$ mole/liter of saccharin in 0.1 N HCl, the diffusion current

* A. P. Poretskaya carried out some of this work.

immediately after the solution has been prepared is $I_{diffusion}$ = 50 μA. If the solution is now stood for 6 hours, the diffusion is found to have dropped to 40 μA. After 96 hours, the diffusion current has dropped further to 34 μA. Results of measurements of the diffusion current of saccharin solutions in acid solution at varying time intervals are shown in Fig. 2 (Curve 1). As Fig. 2 shows, the height of the polarographic wave of saccharin in acid solutions drops rather rapidly. Straight line 2 on the same figure shows that the height of the polarographic wave for saccharin in 0.1 N LiCl remains constant over a long period.

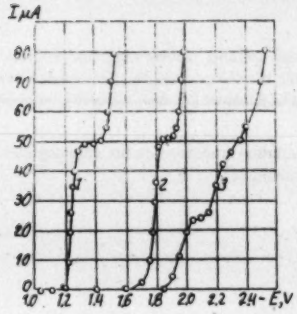


Fig. 1. Examples of polarograms obtained during the reduction of 0.005 mole/liter of saccharin in supporting electrolytes of 0.1 N HCl (Curve 1), 0.1 N NaOH (Curve 2) and 0.1 N LiCl (Curve 3).

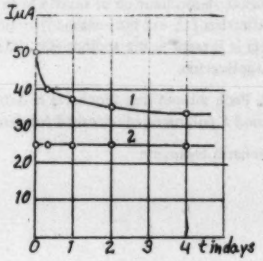


Fig. 2. Stability of saccharin solutions in 0.1 N HCl (Curve 1) and in 0.1 N LiCl (Curve 2), as recorded by change of diffusion current with time.

If, therefore, saccharin is to be determined in acid solution, it is essential to carry out the analysis as quickly as possible; measurement should be carried out within 20-30 minutes of making up the solution.

Quantitative determination of saccharin in neutral solution should be carried out on the basis of measurements of the height of the first wave, which can be determined easily and which hardly changes at all with time.

Fig. 3 illustrated one of the polarograms obtained for solutions of various concentrations of saccharin in 0.1 N LiCl using capillary B.

Wave lengths are proportional to saccharin concentration, as can be seen from examination of Fig. 4, which shows that the calibration curve obtained with capillary B for the determination of saccharin in 0.1 N LiCl is a straight line. This straight line is in agreement with the Ilkovich equation

$$I = 605 \cdot n \cdot D^{1/2} \cdot m^{2/3} \cdot \tau^{1/6} c = 4.3 \cdot c. \qquad (1)$$

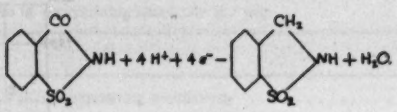
By taking a series of polarograms for solutions of saccharin in 0.1 N HCl we showed that in this case also the wave height is proportional to concentration.

The calibration curve for determination of saccharin in 0.1 N HCl as supporting electrolyte is shown in Fig. 4 (straight line 2).

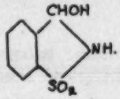
In acid and alkaline solutions, the value of the diffusion coefficient is double that of the diffusion current of the 1st wave for saccharin reduced in neutral media.

Obviously, this is explained by the fact that in acid or alkaline media, $\underline{n} = 4$, while in neutral media $\underline{n} = 2$ for both waves.

This assumption is in good agreement with the results of Matsiu, Sawamura, and Adachi [8], who showed that in acid media, saccharin is reduced according to the equation:



In neutral solution, an intermediate product is probably formed



If it is assumed that on reducing saccharin in acid media $\underline{n} = 4$, then it follows from equation (1) that the diffusion coefficient of saccharin $D = 6.4 \cdot 10^{-6}$ cm²/sec.

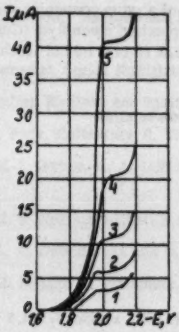


Fig. 3. Polarograms for solutions of 0.6; 1.29; 2.5; 5.0 and 10 mM/liter of saccharin in a supporting electrolyte of 0.1 N LiCl.

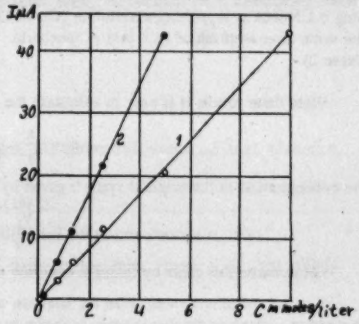


Fig. 4. Calibration curves for determination of saccharin in 0.1 N LiCl (1) and 0.1 N HCl (2). Capillary characteristics $m^{2/3} t^{1/6} = 1.41$ mg$^{2/3}$ sec$^{-1/2}$.

Selection of the most convenient supporting electrolyte for determination of saccharin is determined by what reducing materials are present in solution. The supporting electrolyte should be chosen so that the polarographic wave for saccharin can be separated from other waves in the best possible way. This problem can be solved in a few instances, since the reduction potentials of most materials are shifted by 0.03 V when the pH is changed by one, while for saccharin

$$\frac{dE}{d(pH)} = -0.1 \text{ V}.$$

On the basis of the results obtained, we developed a method for the determination of saccharin in colored syrup added to aerated water. The experiments we carried out showed that saccharin can be determined in syrup in a supporting electrolyte of 0.1 N LiCl or 0.1 N HCl. Saccharin can be determined in this case either by means of a calibration curve, or by the method of additions, or by a combination of the two.

Let us, for example, assume that we have a volume V_s ml of a syrup with a concentration of $\underline{c}$ millimoles of saccharin per liter. We add to this $(V_1 - V_s)$ mls of supporting electrolyte and take a polarogram. Let the height of the polarographic wave obtained I_1 correspond to a content of $\underline{x}$ millimoles of saccharin in V_1 mls. Add $\underline{a}$ millimoles of saccharin, and then make up the volume to V_2 mls and take another polarogram. Let the wave height in this case be I_2.

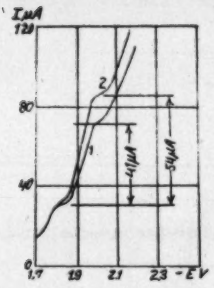


Fig. 5. Polarogram of a syrup containing saccharin using 0.1 N HCl as supporting electrolyte (Curve 1). The same after addition of 14.6 mM of saccharin (Curve 2).

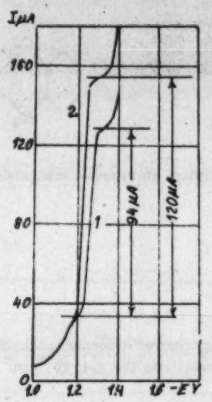


Fig. 6. Polarogram of a syrup containing saccharin using 0.1 N LiCl as supporting electrolyte (Curve 1). The same, after addition of 14.6 mM of saccharin (Curve 2).

From these results it is easy to calculate the saccharin concentration in V_1 mls solution

$$c' = \frac{x}{V_1} = \frac{aI_1}{I_2V_2 - I_1V_1} \text{ mole/liter.} \qquad (2)$$

The concentration in the original syrup is given by

$$c = c' \cdot \frac{V_1}{V_3} = \frac{aI_1V_1}{I_2V_2V_3 - I_1V_1V_3} \text{ mole/liter} \qquad (3)$$

Let us make this clear by taking a concrete case.

$V_3 = 2.3$ ml of syrup was taken for analysis; to this was added 2.5 ml of 0.2 N LiCl, so that $V_1 = 4.8$ ml. The polarogram obtained for this solution is shown in Fig. 5 (Curve 1). The wave height $I_1 = 41$ μA (capillary A was used).

0.2 ml of solution containing $\underline{a} = 14.6 \cdot 10^{-3}$ mM of saccharin was added to the electrolytic cell. The total volume in the cell was then brought up to $V_2 = 5$ ml. Another polarogram was then taken; this is shown in the same diagram (Fig. 2). In this case, the value of the diffusion current $I_2 = 54$ μA.

By substituting these values in formula (3) we get

$$\underline{c} = \frac{14 \cdot 6 \cdot 10^{-3} \cdot 41 \cdot 4.8}{54 \cdot 5 \cdot 2.3 - 41 \cdot 4.8 \cdot 2.3} = 17 \cdot 10^{-3} \text{ mole/liter.}$$

Using the calibration curve for capillary A and reckoning that the syrup has been diluted 2.3/4.8 times, we find from the wave height of $I_1 = 41$ μA that the concentration of the saccharin in the syrup is $\underline{c} = 16.6 \cdot 10^{-3}$ mole/liter.

A similar experiment was carried out with another aliquot of the same syrup. This experiment differed from the one described in that 2.5 ml of 0.2 N HCl was added to 2.3 ml of syrup.

The polarogram for the solution (Curve 1) and the polarogram for the same solution after addition of $14.6 \cdot 10^{-3}$ mM of saccharin (Curve 2) are shown in Fig. 6.

In this case, $I_1 = 94$ μA and $I_2 = 120$ μA.

Results for the determination of saccharin in a syrup by four methods are compared in the table.

TABLE

Comparison of Polarographic Methods of Determining Saccharin in Syrup

Test No.	Method	c, mM/liter	c, g/liter
1	Calibration curve using 0.1 N HCl as supporting electrolyte	17	3.4
2	Calibration curve using 0.1 N LiCl as supporting electrolyte	20	4.0
3	Method of addition using 0.1 N HCl as supporting electrolyte	17	3.5
4	Method of addition using 0.1 N LiCl as supporting electrolyte	19	4.0
	Mean	18	3.7

These results show that the deviation between parallel determinations amounts to 15%. A number of similar determinations carried out by us showed that in most cases, for duplicates, each of the values obtained deviate from the mean by not more than 10%.

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A PERSULFATE-COBALT VOLUMETRIC METHOD OF DETERMINING MANGANESE IN ORES AND ROCKS

D. N. Finkelshtein and I. B. Petropavlovskaya

Central Laboratory of the Ural Geological Administration

The substitution of silver nitrate by cheaper and more readily available catalysts for routine analysis of manganese has attracted the attention of research workers many times. Recently, Kuznetsov and Budanova [1], successfully used a cobalt salt as catalyst. To mask the rose color of the cobalt ion, which hinders observation of the color change at the equivalence point, the authors recommend addition of copper or nickel salts as well, the colors of which are complementary to that of the cobalt ion. The authors showed that the method in which cobalt is used as a catalyst can be applied for the determination of small amounts of manganese in ferrous metals and in alloys with copper and aluminum as bases, respectively. Kulberg, Molot, and Grigoryeva [2], confirmed the results obtained by these authors.

In the present paper we shall show that cobalt catalysts can also be used for the determination of both small and large amounts of manganese in useful ores.

Determination of Small Amounts of Manganese in the Presence of a Cobalt-Copper Catalyst

Experiments were carried out on various types of iron ores (limonite, carbonates, magnetite), complex ores, silicate rocks, and limestones. The analytical conditions for both silver and cobalt-copper catalysts, respectively, were similar.

In practice, permanganate is titrated in the presence of three acids: sulfuric, nitric, and phosphoric acids. Our experiments showed that there is no need to use nitric acid, and that in fact its presence is deleterious, in so far as it slows down oxidation of manganese in the presence of the cobalt catalyst and necessitates additional boiling of the solution to eliminate oxides of nitrogen.

Similar results were obtained whether a solution of catalyst prepared from analytical grade cobalt sulfate or from residues of gravimetric determination of potassium by the cobaltinitrite method were used; the latter was prepared as follows. Filtrate and waste liquors from 30-50 potassium determinations were evaporated in a large basin until a film formed, 100 ml of sulfuric acid (sp.gr. 1.84) was then added, and the mixture evaporated while stirring until white fumes appeared; some water was then added and the whole evaporated further until white fumes appeared again. The precipitate formed was dissolved in hot water, the solution filtered on dilution to ca. 3 liters, cobalt concentration was determined and concentration adjusted to contain 5 g/liter of $CoSO_4 \cdot 7H_2O$. 20 g of cupric sulfate dissolved in the minimum amount of hot water was added per liter of this solution. The catalyst solution thus obtained contained 0.5% $CoSO_4 \cdot 7H_2O$ and 2% $CuSO_4 \cdot 5H_2O$. The residue from one potassium determination is sufficient for 60-70 manganese determinations.

Analytical Procedure

0.5-1 g of finely ground material is placed in a moistened 250 ml flask and 15 ml of aqua regia added and the whole heated. When all evolution of gas has ceased, 10 ml of sulfuric acid (1:1) is added and the mixture evaporated until white fumes appear. Heating is stopped, the walls of the flask rinsed down and evaporation renewed until white fumes appear again. After cooling, 100-120 ml of water and 20 ml of mixed acids (750 ml H_2O + 125 ml sulfuric acid (sp.gr. 1.84) + 125 ml phosphoric acid (sp.gr. 1.7)) are added and the mixture heated till the salts dissolve. 10 ml of catalyst solution is added and 20 ml of a 25% solution of ammonium persulfate; the whole is heated to the boil and kept boiling until the color of permanganate has fully developed, after which the flask is placed in a warm place for 10 minutes to decompose excess persulfate; the solution is then cooled and titrated with arsenite (T = ca. 0.0002 g Mn). To check the result, the titrated solution is heated up again, the manganese oxidized with persulfate and titration repeated after cooling.

TABLE 1

Determination of manganese by the persulfate arsenite method

Material analyzed	MnO found (in %)		
	with a silver catalyst	with a cobalt-copper catalyst	
		in a sulfuric-nitric phosphoric medium	in a sulfuric phosphoric medium
Iron ore No. 1	0.24	0.22	0.23; 0.22
Iron ore No. 2	0.11	0.12; 0.12	0.12; 0.12
Iron ore No. 3	0.04	0.03; 0.03	0.03; 0.04
Complex ore (gabbro with incrustations of titano-magnetite, copper sulfides and apatite) No. 1	0.34	0.34	0.34; 0.35
Complex ore (gabbro with incrustations of titano-magnetite, copper sulfides and apatite) No. 2	0.35	0.35; 0.34	0.35; 0.35
Complex ore (gabbro with incrustations of titano-magnetite, copper sulfides and apatite) No. 3	0.27	0.26; 0.25	0.27; 0.27
Silicate rock No. 1	0.02	–	0.02; 0.015
Silicate rock No. 2	0.05	–	0.04; 0.05
Silicate rock No. 3	0.10	–	0.10; 0.11
Silicate rock No. 4	0.46	–	0.47; 0.48
C.O. 25 and titanomagnetite ore	0.19	–	0.18; 0.19
C.O. 60 and dolomite	0.29	0.28	0.29; 0.30

Table 1, which includes some of the results, shows that the cobalt catalyst can be substituted for the silver catalyst for the determination of small amounts of manganese up to 5-6 mg. The only difference is that oxidation is slower in the presence of cobalt than in the presence of silver; the amount of persulfate is increased by 1.5-2 times (in comparison with the minimum amount necessary when silver is used). When the titrated solution was re-oxidized with persulfate after titrating with arsenite, it was found that in this case oxidation was just as rapid as with a silver catalyst, indicating, therefore, that As enhances the action of the cobalt catalyst; in this respect, arsenic behaves like vanadium and molybdenum [1].

A Study of the Possibility of Using a Cobalt Catalyst for the Determination of Large Amounts of Manganese

Bright and Labaree [3], showed that it is possible to oxidize up to 100 mg of manganese in the presence of silver nitrate and phosphoric acid. Shein and Milkovskaya [4], used this method for the determination of manganese in manganese ores and alloys. These authors recommend addition of sodium formate to prevent precipitation of manganous acid.

TABLE 2

Determination of Manganese in Manganese Ores using Various Catalysts

Mn content (%)		Mn content (%)	
silver catalyst	cobalt-copper catalyst	silver catalyst	cobalt-copper catalyst
52.21	30.90; 31.10	30.70	22.57; 23.34
29.32	22.39; 24.08	6.70	5.40; 4.43; 5.20
29.00	21.30; 21.67	29.32	27.20; 24.27; 25.60
12.18	6.80; 9.20	16.42	14.60; 14.18

Note: The Mohr solutions were standardized by C.O. 51 under the identical conditions, with the same catalysts.

The analyses we carried out on manganese ores using cobalt catalysts (Table 2) show that even comparatively small amounts of manganese are not completely oxidized by this method. Instead of the reddish-violet color characteristic of manganic acid, the solution acquires a red color, which indicate formation of a mixture of manganese compounds in various valency states. Oxidation is slower also in this instance than in the presence of silver salts. The compounds of manganese obtained do not have a standard composition even under strictly controlled conditions, the average valency of the manganese varies within the limits 5.4-6.1 when a cobalt-copper catalyst is used and 5.5-6.3 for a cobalt-nickel catalyst, taking the valency of manganese oxidized in the presence of a silver catalyst as 7. Addition of formate and sulfuric acid do not improve the results. When more than 5% sulfuric acid is present, manganous acid is precipitated.

Good results were obtained on oxidation of high concentrations of manganese in the presence of a combined catalyst consisting of cobalt and a relatively small amount of silver salts (a tenth or a twentieth of the normal

amounts). It is known that for some optimum compositions, i.e., in some freak or lucky cases, it is possible to oxidize manganese to manganic acid in the presence of a minimum amount of silver [5].

TABLE 3

Determination of High Concentrations of Manganese in Ores in a Phosphoric Medium using Various Catalysts

Test No.	Mn found (%)		
	1 ml 0.2% $AgNO_3$	10 ml 0.2% $AgNO_3$	cobalt-copper catalyst with 1 ml 0.2% $AgNO_3$
10010	26.90; 21.32	27.34; 27.63	27.51; 27.36
	24.68	27.63	27.51
10991	23.62; 23.69	23.62; 23.76	23.65; 23.73
	23.62	23.76	23.77
10995	27.31; 27.47	27.51; 27.58	27.45; 27.36
	23.91	27.63	27.63
3703	24.12; 24.32	24.41; 24.52	24.38; 24.46
3708	28.46; 28.92	28.62; 28.92	28.66; 28.73
	27.63	28.92	28.92
C.O. 44	52.35; 52.51	52.48; 52.48	52.48; 52.61
(52.58% Mn)	51.86	52.69	52.48

Experiments show, however, (Table 3) that this technique is not universally applicable, and reliable, poor reproducibility is often the case. In the presence of salts of cobalt and copper, a small amount of silver salt, up to 80 mg of manganese in a volume of 250-350 ml can be rapidly and completely oxidized. There is no need to add formate.

Some of the results obtained for the determination of manganese in carbonate and oxide ores found in a number of locations are given in Table 3.

Analytical Procedure

0.1-0.2 g of finely ground manganese ore is placed in a moistened 500 ml conical flask. 20 ml of phosphoric acid (sp.gr. 1.7) is added and the mixture heated on a hot plate at 300-350° until the dark particles disappear. 200-300 ml of water is added followed by 20 ml of the cobalt-copper catayst, and 1 ml of 0.2% silver nitrate, the whole is heated to the boil and to the hot solution 30 ml of 25% ammonium persulfate solution gradually added. The solution is boiled for 4-5 minutes and then kept in a warm place for 10-12 minutes to destroy excess persulfate. The solution is cooled to room temperature with running water and titrated with a 0.2 M solution of Mohr salt (containing 180 ml concentrated H_2SO_4 per liter) to a weak rose color; 5 drops of 0.1% diphenylaminesulfonate is then added and titration continued until the solution is colorless. Mohr salt was standardized to C.O. 44 or 51.

SUMMARY

1. Cobalt in a sulfuric-phosphoric acid medium can be used instead of silver for the determination of small amounts of manganese in minerals.

2. The cobalt catalyst can only be used for the oxidation of high concentrations of manganese in a phosphoric-sulfuric acid medium when a small amount of silver is present.

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THE USE OF (W_1W_2)-DIAGRAMS FOR X-RAY SPECTROGRAPHIC ANALYSIS

E. E. Vainshtein and I. D. Shevaleevsky

The V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry

Academy of Sciences USSR, Moscow

In recent years some work has been devoted to the use of transposed blackening functions for X-ray spectrographic analysis [1, 2]. A general expression was also derived [3], for this function of which all the formulas suggested previously for transposed blackening functions were special cases. The present article is a development of research along the same direction. We shall characterize the intensity of each of the spectral lines compared during analysis by the values of their arbitrary photo-density $W = \log \frac{1-T}{T}$, where T is the transmittance which is equal to the ratio of the light flow passing through an emulsion, to the light falling on that emulsion. By means of these values, we construct a diagram, which we shall call the W_1W_2 diagram for short. We do this, by changing the exposure, getting a series of spectrograms with lines of varying intensity, and plotting the values of W relating to one of the lines on the abscissa and the value of W corresponding to another, on the ordinate. It was shown recently [4], that in the optical part of the spectrum, lines with an "equal ratio of intensity" for the spectral lines, in the field of a W_1W_2-diagram, for a wide range of values of an "arbitrary photo-density", form a pencil of rays originating from one point, while the relation between W and exposure (E), can be represented by a relation of the following type

$$W = S_0 + aE^b, \qquad (1)$$

with a sufficient degree of accuracy for practical purposes, where W_0, a and b are constants. If the above-mentioned property of (W_1W_2)-diagrams could be experimentally confirmed in the X-ray part of the spectrum, then it could be used for determining the relative intensity of X-ray spectral lines and could serve as a basis for working out a new method of X-ray spectral analysis.

We used the lines of the $K\alpha_{1,2}$ and $L\alpha_{1,2}$ doublets, the ratio of the intensities of which is known to be independent of the conditions of excitation of the spectra, for constructing (W_1W_2)-diagrams. X-ray film of the "Laue" and Soviet XX types were used. The spectrograms were developed in various developers for various times. Development temperature ranged from 16 to 22°. The blackening of the background of spectrograms used for constructing the (W_1W_2)-diagram was not greater than 0.06. One of the W_1W_2 diagrams obtained in the course of the experiments and constructed with the aid of the $K\alpha_{1,2}$ lines of copper (Line 1) and the $L\alpha_{1,2}$ lines of tungsten (Line 2), is given as an example in Fig. 1; this was obtained using a "Laue" film, which was developed in a normal metol-hydroquinone developer at 16° for 6 minutes. Other (W_1W_2)-diagrams constructed with the aid of other X-ray films and developed under different conditions to those described above, are of the same type. Examination of the graphs in Fig. 1 and a comparison of them with others obtained during the present investigation allows one to come to the following conclusions:

1. For changes in the value of W from −1 to +1.8, the lines of "equal ratio of intensity" on (W_1W_2)-diagrams are straight lines in the X-ray part of the spectrum. This range of "arbitrary photo-densities" corresponds to a change in blackening of the spectral lines from values of the order of a few hundredths to a value of ca. 1.8. For larger blackening values of the spectral lines, the shape of the curves of "equal ratio of intensity" on the (W_1W_2)-diagram depart from linearity.

2. The various lines with "equal ratio of intensity" on a (W_1W_2)-diagram intersect at one point, which lies on the bisectrix of the coordinate angle. The coordinates of the "pole" for the films studied in our work were found to be (−3, −3).

3. The position of the pole of the diagram, within experimental error, was found to be independent of development time, and also of the composition and temperature of the developer.

4. With increasing developer contrast, there was observed a small increase in the slope of the straight lines with an "equal ratio of intensity" for the spectral lines. Nevertheless, in practice, this has hardly any effect on the value of the parameters which determine the form of the relationship between W and line intensity.

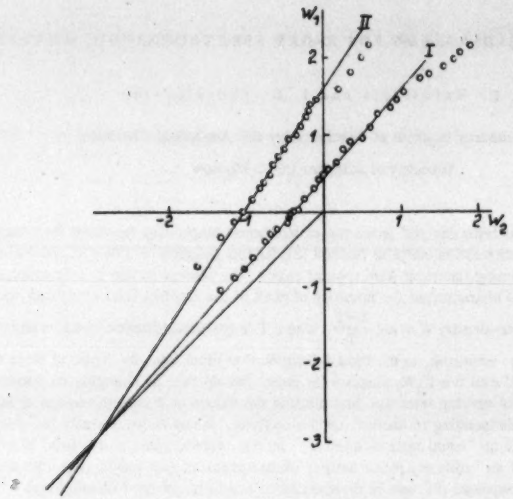

Fig. 1. (W_1W_2)-diagram: Line I) $CuK\alpha_{1,2}$; Line II) $WL\alpha_{1,2}$.

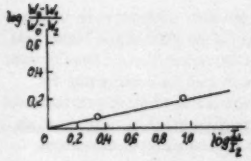

Fig. 2. Graph for the determination of the value of "b" in equation (2).

5. In the part of the spectrum considered (700-1500 XE), the path of straight lines with an "equal ratio of intensity" for the lines on the (W_1W_2)-diagram is independent of the wave length of the radiation.

Since the ratio of the intensities of the lines used for constructing (W_1W_2)-diagrams is known, the results obtained can be used for checking the correctness of equation (1) in the X-ray part of the spectrum, and in the event that equation (1) is shown to be true, the numerical value of coefficient "b" can be determined, a knowledge of which is essential for making practical use of the method in carrying out spectrographic analysis. In actual fact, if equation (1) holds, then for each line with an "equal ratio of intensity" on the (W_1W_2)-diagram, for the whole range of W within which the graphs are straight lines, the following relation:

$$\log \frac{W_1 - W_0}{W_2 - W_0} = b \cdot \log \frac{I_1}{I_2} \qquad (2)$$

should be fulfilled.

Here both the logarithms are known, while b is the constant required. On Fig. 2 values of $\log \frac{W_1 - W_0}{W_2 - W_0}$ calculated from the experimental results are compared with the values of the logarithms of the ratio of intensities of the $K\alpha_{1,2}$ and $L\alpha_{1,2}$ lines. This relation is linear. The value of b calculated from the graph on Fig. 2 was found to be equal to 0.2. Thus, in the W range from -1 to $+1.8$, the function $f(W) = (W - W_0)^b$, where W_0 is a constant (in our case equal to -3), is proportional to line intensity and can be used for quantitative determination of the latter values. For convenience, it is more expedient to present the relation between function $f = f(W)$ and the values of the "arbitrary photo-density" in tabular form.

TABLE

Values of the Function $(W-W_0)^5$ for $W_0 = -3$

W	0	1	2	3	4	5	6	7	8	9
−1.8	2.5	2.4	2.3	2.2	2.1	2.0				
−1.7	3.9	3.7	3.5	3.4	3.2	3.1	2.9	2.8	2.7	2.6
−1.6	5.4	5.2	5.0	4.8	4.6	4.5	4.4	4.3	4.2	4.1
−1.5	7.6	7.4	7.2	7.0	6.7	6.4	6.2	6.0	5.8	5.6
−1.4	10.5	10.2	9.9	9.6	9.2	8.9	8.6	8.3	8.1	7.8
−1.3	14.2	13.8	13.4	13	12.6	12.2	11.8	11.5	11.1	10.8
−1.2	18.5	18.2	17.9	17.4	17.0	16.5	16.0	15.6	15.2	14.7
−1.1	24.8	24.1	23.5	22.9	22.3	21.7	21.3	20.6	20	19.3
−1.0	32	31.2	30.4	29.7	28.9	28.2	27.4	26.8	26.2	25.5
−0.9	40.8	39.8	38.9	38	37.1	36.2	35.3	34.4	33.6	32.8
−0.8	51.5	50.5	49.4	48.3	47.2	46.1	44.8	43.6	42.6	41.7
−0.7	64.6	63.3	62.0	59.1	58.2	57.3	56.4	55.1	53.8	52.6
−0.6	80	78.2	76.5	75	73.5	71.7	70	68.7	67.4	66
−0.5	97.5	95.6	93.7	92	90	88	87	85	83	81.5
−0.4	119.5	116.6	114.2	112	110	108	106	103.9	101.8	99.4
−0.3	144.2	141.3	138.5	136	133.5	130.7	128	125.5	123	121
−0.2	172.5	169	166	163	160	157	154	152	150	147.1
−0.1	206	202.5	199	195.5	192	189	186	182	178	175
−0.0	243	239	235	231	227	223.5	220	216.5	213	209.5
+0.0	243	247.5	252	256.5	261	265	269	273	277	282
0.1	287	292	297	301	306	310	316	322	328	333
0.2	337.5	342	347	352	358	363	369	375	381	387
0.3	393	398	404	410	416	423	430	436	442	449
0.4	456	462	468	475	482	489	496	505	513	521
0.5	530	536	542	547	554	562	571	580	590	598
0.6	605	614	623	631	640	649	659	668	677	687
0.7	698	708	718	727	737	746	756	765	775	785
0.8	794	806	817	829	840	846	862	873	885	895
0.9	905	917	929	941	953	964	975	987	1000	1012
1.0	1024	1037	1050	1063	1076	1090	1104	1118	1132	1146
1.1	1160	1174	1188	1203	1218	1232	1246	1260	1274	1288
1.2	1302	1319	1336	1354	1372	1390	1407	1424	1441	1458
1.3	1475	1492	1509	1526	1543	1560	1578	1596	1614	1632
1.4	1650	1670	1690	1710	1730	1750	1770	1790	1810	1830
1.5	1850	1870	1890	1910	1930	1950	1971	1992	2015	2037
1.6	2060	2084	2108	2132	2156	2180	2203	2226	2249	2272
1.7	2295	2321	2347	2373	2399	2425	2451	2477	2503	2529
1.8	2555	2581	2607	2633	2659	2685	2714	2743	2772	2801
1.9	2830	2854	2878	2902	2926	2950	2985	3020	3055	3090
2.0	3125	3160	3195	3230	3265	3300	3331	3362	3393	3424
2.1	3455	3490	3525	3560	3595	3630	3664	3698	3732	3766
2.2	3800	3840	3880	3920	3960	4000	4040	4080	4120	4160
2.3	4200	4240	4280	4320	4360	4400	4440	4480	4520	4560
2.4	4600	4644	4688	4732	4776	4820	4866	4912	4958	5004
2.5	5050									

In comparing line intensities, strict calculation of the spectrogram background can be carried out by means of the relation

$$(W_L - W_0)^5 = (W_{L+B} - W_0)^5 - (W_B - W_0)^5, \qquad (3)$$

in which W_L corresponds to the peak of the line after calculating the background; W_{L+B} corresponds to the peak of the line before taking into account the background, while W_B corresponds to the background of the spectrogram.

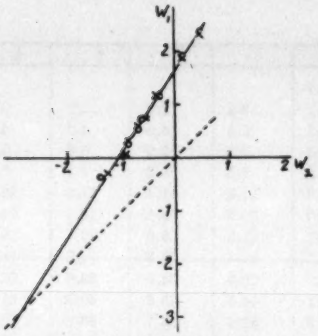

Fig. 3. (W_1W_2)-Diagram: o = background calculated according to Equation (3); x = background by approximate calculation.

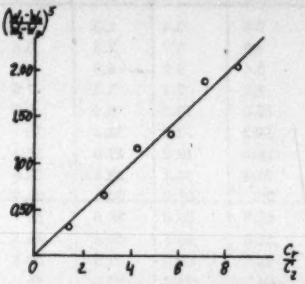

Fig. 4. Relation between $\frac{W_1 - W_0}{W_2 - W_0}$ and concentrations of test and reference elements.

Nevertheless, as we proved, calculation of the spectrogram background can be realized more simply by subtracting the value corresponding to it from the blackening of the line and then transforming to W values. This is illustrated by the graph shown in Fig. 3. Here, the circles represent points obtained by a strict calculation of background according to formula (3), while the crosses correspond to points obtained by approximate calculation. It is obvious that both sets of points lie practically on the same straight line.

Hitherto, only the first results have been obtained which characterize the possibility of making practical use of the method of analysis described. Thus, its use for the analysis of zirconium minerals has permitted major components to be determined with an accuracy of ca. 5-6%. The calibration curve, which in this case expresses the relation between the values of $\left(\frac{W_1-W_0}{W_2-W_0}\right)^5$ and the concentrations of test element and reference element, respectively, is shown in Fig. 4. There are grounds for assuming that (W_1W_2)-diagrams may be used for solving many other problems.

Received October 6, 1954

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BRIEF COMMUNICATIONS

A SPECIFIC REACTION FOR VANADIUM

V. L. Zolotavin

The S. M. Kirov Ural Polytechnical Institute

The reduction of sexivalent molybdenum to so-called molybdenum blue is used for the determination of a number of ions (Sn^{2+}, Ce^{3+}, and others). There is more than one point of view on its composition [1-5]; most research workers are inclined to assume that molybdenum is present in different valency states in this compound, in particular in the quinquevalent state. This assumption explains the formation of molybdenum blue by the action on ammonium molybdate of such reducing agents as the salts of Cu^{+}, Sn^{2+}, hydrogen sulfide, sulfur trioxide, etc.. In reference books [6], data is given for the value of the normal oxidation-reduction potential of the system

$$\varepsilon_{MoO^{3+} + 2H_2O \,/\, MoO_3 + 4H^+} = 0.5 \text{ V}.$$

A comparison of this value with the analogous one for tin ($\varepsilon_0 = 0.15$ V) confirms the assumption made above.

The aim of the present investigation was to study the possibility of using the reaction discussed above for the detection of vanadium present in solution in the form of ions in a low valency state; we started off on the basis that the normal oxidation reduction potentials of the system V^{2+}/V^{3+} and $V^{3+} + H_2O/VO^{2+} + 2H^+$, are, respectively -0.20 and 0.314 V more negative than the normal potential of the system $MoO^{3+} + 2H_2O/MoO_3 + 4H^+$. As for the system $VO_3^- + 4H^+/VO^{2+} + 2H_2O$, its normal potential, which is equal to 1.0 V, depends to a considerable extent on hydrogen ion concentration, and consequently, can be easily lowered to such a value at which vanadium ions can reduce sexivalent molybdenum to the quinquevalent state.

EXPERIMENTAL

Solutions of the salts of di-, tri-, quadri- and quinquevalent vanadium were used. A saturated solution of commercial ammonium molybdate was the reagent used.

Tests showed that V^{2+} and V^{3+} ions reduced sexivalent molybdenum to molybdenum blue only in a strong acid medium, at a pH not greater than 2; the reaction under these conditions is very rapid. Vanadium ions can effect this reduction in a weak acid medium at pH 4.0-4.5. This pH is obtained by putting a piece of Congo indicator paper in the solution and adding 1-2 N alkali solution dropwise until the color of the paper changes to reddish violet. At this pH, the reaction is slow and sometimes the blue color does not appear immediately; the solution is first colored violet, which changes subsequently to pure blue.

The sensitivity of the given reaction for pure salts amounts to 0.003 mg in one drop with a volume of 0.05 ml for di- and tri-valent vanadium, and 0.015 mg in 0.05 ml for quadrivalent vanadium.

On the basis that the reaction sensitivity in the first instance is double that in the second, it was found expedient to use metallic zinc as the reducing agent, since it reduces vanadium to the divalent state. There was no reason to fear a rapid change over of the latter into the trivalent state since V^{3+} has the same effect as V^{2+} on sexivalent molybdenum. Further oxidation of V^{3+} into VO^{2+} is comparatively slow. The given reaction was checked on mixtures containing all the cations studied in the ordinary course of qualitative analysis, and also in the presence of titanium, uranium, thorium, zirconium, and cerium. It was demonstrated experimentally that after treating the solution with metallic zinc, Ti^{3+} and U^{4+} ions have the same effect as vanadium ions on ammonium molybdate.

The following procedure is recommended for carrying out this reaction for vanadium: to 2-3 ml of test solution ammonia is added dropwise until a faint turbidity ensues, this is removed by careful addition of 2 N acid solution. Zinc powder is added to the test tube and the tube shaken until gaseous hydrogen ceases to be evolved; care is taken to ensure that zinc is always present in excess. The whole is filtered and 0.5 ml of filtrate added to the same volume of a saturated solution of ammonium molybdate (if turbidity occurs at this stage, the solution should be slightly acidified). Appearance of a blue color indicates the presence of vanadium. The reaction takes 5-7 minutes. The reaction only occurs in sulfuric or hydrochloric acid solution.

Substitution of ammonium molybdate by phosphomolybdic acid showed that when the latter is used the sensitivity of the reaction decreases appreciably.

SUMMARY

1. A reaction has been developed for vanadium which can be used for detecting the latter in the ordinary course of qualitative analysis, and is based on reduction of sexivalent molybdenum to molybdenum blue by V^{2+} and V^{3+} ions.

2. This reaction can be used in the presence of all cations studied in ordinary qualitative analysis, and also in the presence of cerium, thorium and zirconium. Ti^{3+}, U^{4+}, and NO_3^- interfere.

3. By regulating the pH during the reaction, it is possible to distinguish V^{2+} and V^{3+} ions on the one hand, and VO^{2+} ions on the other.

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* Soviet analytical chemistry has introduced a term — "Drobnyi Analysis" — which is defined as follows: "The detection of ions by specific reagents in tests carried out in an arbitrary order, on separate portions of test solution, is called drobnyi analysis". This term has been translated as "fractional analysis" in this paper. Publisher.

COLORIMETRIC DETERMINATION OF THE QUALITY OF AZORIBAMIN

V. M. Iosikova

The All-Union Scientific Research Vitamin Institute, Moscow

Difficulties crop up during estimation of the quality of azoribamin, one of the intermediate products in riboflavin synthesis, since existing methods of determining azo dyes by reduction of the azo group with stannous chloride and titanium is inconvenient for routine analysis, and in the case of azoribamin, the method does not give sufficiently accurate results.

Nevertheless, on comparing analytical results at our disposal on samples of azoribamin with other indices of its quality (melting point, reduction with stannous chloride, etc.), we became convinced that in these samples there were yellow contaminants which lead to high results for the colorimetric analysis.

Azoribamin is insoluble in cold benzene; by treating samples of azoribamin with benzene in the cold, we found that this solvent extracted the yellow contamination; it proved to be products which do not submit to diazotization during the technical process. We found up to 85% of these compounds in some samples, this led us to suggest a double treatment of the test samples, with subsequent measurement of the color of the solutions as a method of estimating the quality of azoribamin.

The following procedure was developed: 2 lots of 20 mg samples of each sample of azoribamin are taken. One is dissolved in acetone (20 mg/100 ml), the other, in cooled benzene (20 mg/100 ml); both solutions are filtered. The necessary volumes of each filtrate are used for filling the cells of a photocolorimeter and the colors of the solution measured with a filter of λ 470 mμ. By using a calibration curve constructed with the aid of pure, 100% azoribamin, the dye content of the first and second filtrates can be determined. In the first instance, we get the sum of the dyestuffs, in the second, the amount of contaminant. By subtracting the second value from the first, we get the percentage of azoribamin in the test solution.

TABLE

Analysis of Azoribamin Samples

Test Number	Sample	M.p. of original azoribamin	Azoribamin content (%)	Contamination (%)	M.p. after removal of contamination
1	Azoribamin 8 a.	164.0	86.0	6.5	167.5
2	" 8 b.	167.5	90.0	3.5	170.0
3	" 9	168.0	95.0	2.4	170.0
4	" 10.	167.0	90.0	5.5	168.5
5	" 11 a.	165.5	80.4	7.0	167.5
6	" 12.	159.5	71.0	8.5	166.5
7	" 13.	164.5	79.5	6.5	167.5
8	" recrystallized.	172.0	95.5	1.5	172.0
9	" twice recrystallized. .	172.0	97.5	2.5	172.5

This method is extremely simple and is convenient for production control as an "express" method in routine analysis. We checked on a large number of azoribamin samples by means of it. Some of the results obtained are given in the table.

The method just described for the determination of the quality of azoribamin is included at present in the instructions in techno-chemical control of the production of synthetic riboflavin.

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OBSERVATIONS MADE BY K. MITSKA AND A. A. VLCHEK [1], REGARDING THE ARTICLE "DIFFUSION OF ELECTROLYTES AND THE POLAROGRAPHIC METHOD"

Ya. P. Gokhshtein

The basis of quantitative polarography is the Ilkovich equation which only takes into account radial diffusion to the drop surface. The effect of agitation of the liquid on the progress of ions to the electrode, discovered by many research workers, makes the values of diffusion coefficients obtained by means of the Ilkovich equation somewhat unreliable. The extent of the deviation of the coefficients, as calculated from this equation, from the actual value D can be determined by any independent method (under conditions where the method is valid).

The conclusions reached in [2], which touch upon this question have drawn some observations from K. Mitska and A. A. Vlchek which are contained in their paper [1]; this paper consists of two parts. The first part contains the conclusions given in [2], in a somewhat inaccurate form, while the second part consists of the authors' observations regarding these conclusions. In the first and second conclusions (first part of [1]) "it is stated that "the limiting polarographic current consists of a diffusion current (the Ilkovich current) and a supplementary current (which is not taken into account in the Ilkovich equation), whose value amounts to on an average of 23% of the diffusion current . . . ".

$$I_{limiting} = I_{diffusion} + 0.23 I_{diffusion}.$$

Even the most careful study of this sentence cannot enable one to interpret it as a statement to the effect that the supplementary current is a part of the Ilkovich diffusion current. Nevertheless, it is precisely this interpretation that is put on it in the second part of article [1]: "Gokhshtein states that the supplementary current does not obey the Ilkovich equation, and at the same time regards it as a part of the Ilkovich diffusion current, which is an obvious contradiction". By this same statement, Mitska and Vlchek admit an obvious contradiction in their own paper.

These authors consider that the diffusion coefficients obtained by the diffraction micro-method are wrong, and to support their argument give tables containing results by Stackelberg, Nernst, and Skobets ([1], p. 2). The agreement between the results of Stackelberg-Skobets and the theoretical values of Nernst, holds only at infinite dilution. Before they talk of inaccuracies in [2], therefore, these authors must first make sure that the Nernst equation represents the real diffusion in solution; their criticism is only valid in so far as the Nernst equation is correct. What's more most of Stackelberg's results proceed from a modified Ilkovich equation and are a consequence of this equation.

Naturally, the conclusions drawn from an equation never contradict the very equation they are derived from. To verify the original equation by deductions made from it would be mathematically false. Nevertheless, this is just what Mitska and Vlchek proceed to do in their paper: "The Ilkovich equation agrees with experimental results, if the values obtained by Stackelberg and his coworkers for the diffusion coefficients are substituted in this equation." This should, in the opinion of the authors confirm the Ilkovich equation.

The accuracy of the Ilkovich equation in practice, cannot be proved by the means used by Mitska and Vlchek. The conclusions drawn by them from this proof are erroneous. It is clear that the results they obtained by means of this doubtful method, do not contradict, but rather vindicate by the very fact that they disagree with them. the results obtained by the diffraction method.

Which values of the diffusion coefficients are right or wrong should be decided, not by the number of authors, so much as by the number of methods of determining them, and by an analysis of each of these methods.

The authors (Mitska and Vlchek) by confining themselves to the use of Stackelberg and Skobets' results fail to pay any attention whatsoever to the diffraction method with which they do not agree. It has as many possibilities as other methods, and has a number of advantages over them. What it is based on has been discussed in [2]. Check tests obtained in the course of this work (see Table 1), agree with the generally accepted results obtained by Harned using the method of electro-conductivity. The accuracy of the diffraction method has also been noted in the articles of Panchenkov and Levina [3], and Khakin [4].

Real diffusion coefficients take into account the effect on the current of those processes which are not taken into account in the Ilkovich equation. Thus, there appears in this equation an empirical factor of 1.23. The latter,

which is a generalization of more complicated functional relationships, has its limits of application. They have been shown to be fairly wide in [2].

The questions which have given rise to doubts on the part of Mitska and Vlchek are considered in more detail below.

I

Mitska and Vlchek state that there are no grounds for the development of a supplementary current. Nevertheless, it has been established by many authors that the assumptions made in deriving the Ilkovich equation render it insufficiently accurate for reproducing the complex phenomena which accompany electrolysis.

Strehlow, Stackelberg and Kuteckey[5], have pointed out the inaccuracy which is the outcome of the assumption that the thickness of the diffusion layer is negligibly small compared with drop radius. The Ilkovich equation does not take into account the tangential movement of the drop surface [6]. It can be caused by non-uniform polarization of the drop, by the discharge of the mercury from the capillary and by drop growth.

Addition to the solution of surface active materials only decreases agitation of the electrolyte (Lingane and Loveridge [7]).

Taylor, Smith, and Cooper [8], while studying the change in current during the life of one drop, found that deviations from the Ilkovich equations are apparent right up to the moment when the drop breaks off.

In deriving the Ilkovich equation it has been assumed that, beyond the limits of the diffusion layer, the concentration of the material is constant and equal to the concentration of the solution as a whole, i.e., it is assumed that there is complete mixing of the solution after each drop breaks off. Experiments carried out by Kryukova [9], (electro-reduction of oxygen dissolved in 1 N KCl in the presence of phenol red indicator) showed that the impoverished layer attains an appreciable size and that the drops produce agitation only in the impoverished layer, which is accordingly not broken down by agitation and increases with each drop. Similar experiments were carried out by Kemula and Grabowsky [10], during a study of the effect of oxygen waves on the waves which follow them.

Stackelberg [11], introduced a correction for this effect of impoverishment. The "annexation" effect was not taken into account by Stackelberg because of the impossibility of determining it theoretically or experimentally.

It is clear that electrolysis occurs in conditions which are far from ideal. Some of the deviations from the ideal case increase the current, others lower the current. It would be a mistake to see in a partial or even complete compensation of the effects of these deviations on the current, an approach to ideal conditions. Compensation does not mean exclusion of components of these deviations from the value of the current. Let us assume that the current is decreased because of the impoverishing effect and increases as a result of convection diffusion. Does this mean, that for complete compensation, the current will consist wholly of a radial diffusion current? No. As a result of impoverishment, the share of the radial diffusion current decreases, with agitation the contribution of the supplementary current increases, and consequently, the division of the current into ordinary and supplementary currents increases.

II

1) Vlchek [12], states that the Ilkovich equation is exactly fulfilled for a rate of discharge of mercury of $\underline{m}$ = 2 mg/sec when 8 conditions are observed. These conditions strongly restrict the range of investigation and Vlchek's experiments become almost special cases. One of these conditions talks about "the use of a discharging material which excludes agitation". Thus Vlchek subdivides discharging materials into those which "exclude" and those which "do not exclude" agitation. Such a division is unknown. If one assumes that such a division is possible, then Cd^{2+}, which Vlchek used, does not exclude the appearances of a supplementary current, the reason for which seems to be agitation of the electrolyte. From T. A. Kryukova's results [6], it is clear that $I_{supplementary}$ for Cd^{2+} attains an appreciable value.

A criticism of Vlchek's statement is contained in a paper published recently by Hans, et. al. [13]. In particular, it is shown there that the maximum of the second type (for Cd^{2+}, Tl^{+}) occurs even at $\underline{m}$ = 1 mg/sec, while according to Vlchek agitation is absent even at a discharge velocity of $\underline{m}$ = 2 mg/sec. The equation given by Hans, et. al. for the diffusion current differs appreciably in the value of its factor from the Ilkovich equation, but is similar to the one in article [2].

2) In proving the accuracy of the Ilkovich equation at $\underline{m}$ = 2 mg/sec, Vlchek used the value of $D_{Cd^{2+}}$ found by Stackelberg for $\underline{m}$ = 4 mg/sec. Gelatin (0.01%) which was present in Stackelberg's experiments, on the one hand decreases differences in tangential movements, but on the other hand it does not satisfy one of Vlchek's conditions,

according to which the solution should not contain surface active materials.

3) Stackelberg determined $D_{Cd^{2+}}$ in 0.1 N KCl ($D_{Cd^{2+}} = 0.728 \cdot 10^{-5}$ cm²/sec). Vlchek used 0.1 M H_2SO_4 as the medium. Here, apparently Vlchek reckons that $D_{Cd^{2+}}$ in 0.1 N KCl is equal to $D_{Cd^{2+}}$ in 0.1 M H_2SO_4. Let $D'_{Cd^{2+}} = \varphi_1(C_{KCl})$ and $D''_{Cd^{2+}} = \varphi_2(C_{H_2SO_4})$. Then a strictly defined pair of values of C_{KCl} and $C_{H_2SO_4}$ will correspond to this value of $D'_{Cd^{2+}} = D''_{Cd^{2+}} = 0.728 \cdot 10^{-5}$ cm²/sec. There is no basis for assuming that this pair will be precisely $C_{KCl} = 0.1$ M and $C_{H_2SO_4} = 0.1$ M.

4) In comparing theoretical values with experimental ones, Vlchek also used an ideal value of $D_{Cd^{2+}}$ (according to Nernst), which slightly exceeds $D_{Cd^{2+}}$ under actual experimental conditions.

III

If, in the presence of excess supporting electrolyte the cation does not form an anionic complex, then its diffusion coefficient will be significantly lower than at infinite dilution. Vinogradov and McBain came to this conclusion [14], after studying the diffusion of ions in a mixture of electrolytes by means of a porous diaphragm method. We give the results below expressed in terms of cm²/sec. (See Table 1).

Work carried out by Kabanov [15], led to the same conclusion. He studied the diffusion of hydrogen ions in various media using a rotating copper amalgamated disc electrode. (Calculations were based on V. G. Levich's theory.)

TABLE 1

Diffusion Coefficients of Each Ion in 0.426N $BaCl_2$ to which Increasing Amounts of HCl have been Added

C_{HCl} / $C_{1/2BaCl_2}$	$D_{Ba^{2+}} \cdot 10^5$ cm²/sec	$D_{Cl^-} \cdot 10^5$ cm²/sec	$D_{H^+} \cdot 10^5$ cm²/sec
0.0235	1.16	1.30	10.84
0.12	0.91	1.59	9.75
0.12	1.14	1.71	9.83
1.2	0.54	2.56	4.82
	0.56	2.62	4.86

TABLE 2

Effect of Nature and Concentration of the Indifferent Electrolyte on the Value of the Real Diffusion Coefficients of the Hydrogen Ion (from Kabanov's article)

Electrolyte composition	$D_{H^+} \cdot 10^5$ cm²/sec	From 9.34 (%)
Infinitely-dilute solution	(according to Nernst's equation) 9.34	100
$2 \cdot 10^{-3}$ N HCl + 0.1 N KCl	7.40	79
10^{-3} M H_2SO_4 + 0.05 M K_2SO_4	4.20	45
10^{-3} M H_2SO_4 + 0.25 M Na_2SO_4	2.80	30

It is clear from Table 1 that $D_{Ba^{2+}}$ and D_{H^+} decrease, respectively, by 52 and 56%. It follows from Table 2 that D_{H^+} in 0.25 M Na_2SO_4 is 3.37 times less than D_{H^+} in 0.1 N KCl. Dean got the same results [16], while studying the diffusion of ions in indifferent electrolytes. It is also necessary to refer to Rulfs' work as well [17], whose results directly confirm results obtained by the diffraction method. Rulfs determined the diffusion coefficients of Pb^{2+}, Cd^{2+}, Tl^+ by means of an electrolyzer with a porous diaphragm which ensured non-mixing of the electrolytes. His results, compared on the one hand with those of the diffraction method, and on the other hand with Stackelberg [18], permit one to assess the statement by Mitska and Vlchek to the effect that the results of the diffraction micro-method contradict results obtained by other authors (Table 3).

TABLE 3

Medium	Ion	$D \cdot 10^5$ cm² · sec⁻¹			
		Gokhshtein (diffraction micro-method)	Rulfs	Stackelberg	Nernst
0.1 M KCl	Pb^{2+}	–	7.5	8.65 (8.69)	9.8
1 M KNO_3	Pb^{2+}	6.82	6.7	8.02	9.8
0.1 M KNO_3	Tl^+	15.1	16.7 (15.2)	18.2	20
1 M KCl	Cd^{2+}	5.22	–	7.89	7.2

It is obvious that Rulfs' results confirm (with an accuracy of up to 2%) results obtained by the diffraction micro-method, despite what Mitska and Vlchek say, and differ (by up to 20%) from those of Stackelberg, which Mitska and Vlchek uphold. Rulfs in his article emphasizes that the diffusion coefficients of Cd^{2+}, Pb^{2+}, Tl^+, obtained by calculation from Strehlow and Stackelberg's equation, and by Cottrel's method are in poor semiquantitative agreement with his results.

The porous diaphragm method can be relied on; it is enough to point out its agreement in the case of salts with the conductometric method [19].

Thus, after getting acquainted with the work of a number of other authors, and also with the methods used by Mitska and Vlchek as proof of their allegations, it is clear that their statement regarding the errors of the diffraction micro-method is incorrect. At the moment, up to 10 very different methods for determining D are in existence; they differ considerably, however, from each other with respect to accuracy. The polarographic method,* which gives high results for D, is surpassed in this instance by the capillary method (Wang [20]), whose values exceed that of the polarographic method by 12-30%. Such a coincidence in the sign of the deviation cannot serve as a proof that these methods give reliable results.

Now let us touch briefly on the deviation between results obtained on a stationary solid electrode and those of independent methods. The reason for such discrepancies is side effects which accompany electrolysis on solid stationary electrodes and the consequent inaccuracies of this method of determining diffusion coefficients. We list below these side effects which affect current strength.

1) In experiments carried out by Stackelberg and coworkers [18], who used a disc electrode with a comparatively large area ($q = 0.1307\ cm^2$), as a result of electrode reactions on the electrode surface density gradients arise which lead to agitation of the electrolyte. As a consequence of this mixing, the flow of diffusing material to the electrode surface, and consequently current strength is greater than in the case when there is only linear diffusion. A paper published recently [21], confirms the existence of natural convection during electrolysis on solid stationary electrodes.

2) No account is taken of the effect of changes in electrode surface on the current as a result of deposition of electrolysis products.

3) In Stackelberg et. al, experiments, they did not take into account the effect of dissolved atmospheric oxygen on the value of the diffusion current either. Solid electrodes are known to be very sensitive to traces of atmospheric oxygen. It is very difficult to remove traces of dissolved oxygen which is reduced on the electrode, thereby increasing the current, from 120-150 ml.

The method adopted by Skobets and Kavetsky [22], of a current throw on spherical, amalgamated, stationary electrodes and on stationary wire electrodes does not avoid the snags enumerated above which are associated with the use of solid electrodes.

IV

The fact that a supplementary current exists, means that a correction must be applied to formulas which do not take this fact into account. The Heyrovsky-Ilkovich equation for I^0/I, and also the more complex formulas of Kolthoff and Lingane, and of McGilvray, respectively, are true only in a qualitative sense. When, however, they are tested quantitatively they are found to disagree with experimental results. The results of Kolthoff and Lingane may be used as an illustration [23].

TABLE 4

Comparison of Initial Limiting Currents and Diffusion Currents of Reduced Ions (Kolthoff and Lingane's Results)

Test No.	Reduced salt	I^0 (μA)	I (μA)	n_I^0	Ratio I^0/I				
					observed	calc'd for H-I equation*	% relative to observed value	calc'd from the K-L equation**	% relative to observed value
1	0.001 M TlCl	11.6	6.10a	0.500	1.90	2.00	105	2.00	105
2	0.0013 M TlOH	13.9	8.15b	0.277	1.71	1.39	81	1.66	97
3	0.0026 M TlOH	26.7	15.85a	0.277	1.69	1.39	82	1.66	98
4	0.0026 M $TlC_2H_3O_2$	34.2	15.85a	0.646	2.16	2.83	131	2.37	110
5	0.0005 M $TlIO_3$	6.55 (Tl^+)	3.30a	0.646 (Tl^+)	1.99	2.83	142	2.37	119
6	0.00095 M $PbCl_2$	17.6	8.35a	0.483	2.11	1.93	91	2.39	113
7	0.00095 M $PbCl_2$	17.6	8.00b	0.483	2.20	1.93	88	2.39	109
8	0.001 M $CdSO_4$	12.7	8.00a	0.400	1.59	1.67	105	1.83	115
9	0.00015 M KIO_3	2.40 (IO_3^-)	3.70a	0.356 (IO_3^-)	0.65	0.74	114	0.84	129

a) in 0.1 N KCl, corrected for residual current.
b) in 0.9 N KCl, corrected for residual current.

* It is understood that in this case the diffusion coefficients are calculated according to the Ilkovich equation.
** Heyrovsky-Ilkovich equation.
*** Kolthoff-Lingane equation.

It is difficult to say whether the supplementary current is the only reason for this disagreement; it is, however, perfectly obvious, that the theoretical value of I^0/I and the experimental value $\frac{I^0 + I_{supplementary}}{I + I_{supplementary}}$ will differ, particularly if $I_{supplementary}$ is appreciable. The experimental results [2] are in complete agreement with Kolthoff and Lingane's results. We are, therefore, discussing deviation between objective experimental results and the equation for I^0/I. Since these deviations, with the exception of 2 experiments, exceed 9% and get as high as 42%, it is natural to conclude that this equation has not been experimentally verified as pointed out in [2].

If it is reckoned that formula $\frac{I^0}{I} = \frac{1}{1-n_0}$ is accurate, then the experimental results obtained for I^0/I, show that n_0 should be 20-30% (not more than 35-40%) lower than the transport number obtained at infinite dilution. Thus, in the case of 0.0005 M $TlIO_3$, n_0 at infinite dilution is 0.646, while on substituting the experimental value of $I^0/I = 1.99$ in the equation $\frac{I^0}{I} = \frac{1}{1-n_0}$, the latter gives a value of $n_0 = 0.498$, which is 30% less than 0.646.

If it is considered that I^0/I depends exclusively on n_0, then in order that there should be agreement with experimental results, it is necessary to apply a correction to n_0, since this brings in deviations from the conditions for which the equation was derived. This was shown in [2], taking formula (4) as an example. The presence in the article of this formula derived by auxiliary functions, does not testify to any objection to a rapid decrease in transport number. On the contrary it was emphasized on two occasions in this article, that a theory based "on the assumption that the migration current is lowered exclusively as a result of a rapid decrease in transport number", has not been verified experimentally. It was also shown in [2], that the migration current cannot explain the origin of the supplementary current, which must, therefore, be regarded as resulting from mixing, and is capable of being taken into account in deriving an equation for I^0/I. It is clear from this that the author of [2], did not deny a rapid decrease in transport number, and consequently tends to equate it to zero; rather he reckons that it is one of the factors influencing the migration current, one – but not the only one.

In pointing out the accuracy of the equations for I^0/I, Mitska and Vlchek write that the formulas of Heyrovsky, Kolthoff and McGilvray are in good agreement with experiment.

Since these equations differ essentially from each other, they cannot all at the same time be in good agreement with experimental results. Kolthoff's formula contains the factor $\left(\frac{D_{salt}}{D_{ion}}\right)$ while McGilvray's formula in addition to this contains another factor $\frac{\delta_0}{\delta_+}^{1/3}$ for changes in diffusion coefficient in the presence of indifferent electrolytes (supporting electrolyte). The theory of solution cannot, at present, define exactly the value of this correction; neverthe-

TABLE 5

Comparison of Experimental Values for the Diffusion Current Constant (K_p)* for Some Ions, $t = 25°$ C

Reduced salt	Supporting electrolyte	$K_p = \frac{I_{limiting}}{cm^{2/3} t^{1/6}} \frac{\mu A}{m\,mole/liter}$		
		Strehlow and Stackelberg	Kolthoff and Lingane	Gokhshtein [2]
$CdCl_2$	1 M KCl	3.44; 3.45	3.58	3.50
	0.1 M KCl	3.58	3.51	3.35
$CdSO_4 \cdot {}^8/_3\, H_2O$	1 M Na_2SO_4	–	–	2.79; 2.80
or other cadmium salts	0.5 M H_2SO_4	–	2.60	–
$Pb(NO_3)_2$	1 M KNO_3	3.98; 3.88	3.80	3.83; 3.85
	0.1 M KCl	3.84; 3.89	3.86	–
	1 M NaOH	–	3.39	3.57

* K_p – the constant found polarographically.

less, changes in the diffusion coefficient (see above) show that it is significant. In view of this correction it is inadmissible, in the presence of a supporting electrolyte, to use diffusion coefficients calculated according to Nernst, since this would mean ignoring a large though undetermined factor. Mitska and Vlchek, reckoning the equation of McGilvray's to be true and consequently the correction $\frac{\delta_0}{\delta_+}^{1/2}$, at the same time use values of D calculated from Nernst's equation [12]. It is obvious that the question of the real diffusion coefficient is of first rate importance for the equation I^0/I also. In conclusion, we must point out the lack of foundation for the allegation made by Mitska and Vlchek that "the experimental results of [2], contradict results obtained by other authors". This statement has already been shown above

to be untrue in the case of diffusion coefficients, that it is also incorrect with regard to diffusion currents is demonstrated by the results given in Table 5.

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* See Consultants Bureau Translation, page 77.

C H R O N I C L E

LEONID MARKOVICH KULBERG

(1912-1955)

On the 8th of February, 1955 Professor Leonid Markovich Kulberg died in Saratov. He was a talented Soviet chemist, a member of the Commission on Analytical Chemistry of the USSR Academy of Sciences, the head of the Department of Analytical Chemistry in Saratov University, and a doctor of chemical sciences.

L. M. Kulberg was born on the 15th of December, 1912 in Kiev. He received his primary education in a trade school and in a chemical technical school; from the fourth year at the technical school he went into the chemistry faculty of Kiev University, where he finished in 1935. During the time he was a student, Kulberg showed a great interest in research activity and up to the time when he finished at the University, he had already published 15 papers.

This early work of his which dealt with the analytical use of organic oxidation-reduction systems is well-known.

His most important work was devoted to the theoretical and practical application of organic compounds in mineral analysis, and to the development of spot techniques directly connected with their use.

His work is a serious contribution to the chemistry of organic reagents. The theory which he developed on functional-analytical, and analytically active groups has enabled many disconnected experimental facts to be systematized.

Some of his ideas have an important all-round scientific significance; they are widely used in scientific literature. They have been echoed in foreign literature. This is clearly demonstrated by the publication of a Czech translation of his monograph on "Organic Reagents in Analytical Chemistry".

During his 20 years of independent research, Kulberg published over 150 papers and received a number of authors' acknowledgements. His work has appeared in 27 different scientific journals; he has taken an active part in compiling symposiums and proceedings. He has written a number of monographs on various branches of chemistry.

Although his main field has been analytical chemistry, he has also carried out work in preparative, pharmaceutical, medical and other fields in chemistry; some special preparations including an important antituberculer preparation have been developed by him, and he has suggested methods of analyzing biological materials.

A characteristic feature of his scientific achievements has been the inner-unity in setting up and developing serious theoretical problems and their subsequent practical solution on actual problems. Examples of this are the large number of reagents which he used for solving individual analytical problems, the new methods of analysis, and fields of application of known or modified methods, which have now to varying extents been taken up by industrial, scientific and educational laboratories. L. M. Kulberg developed a method of synthesizing biologically active preparations; his monograph on "Spot Analysis" is an encylopedia on this particular analytical technique. Our friends in China value the practical significance of this book highly and have translated the section devoted to spot tests for minerals; in addition, they have also translated a number of other articles by him which have appeared in our own chemical journals.

Kulberg combined intensive research and publishing work with a large amount of teaching practice. Up to his last days, he was enthusiastically carrying out social and organizational scientific work. He was deputy chairman of the Praesidium of the Saratov Section of the D. I. Mendeleev All-Union Chemical Society, and participated in the work of the USSR Academy of Sciences Analytical Commission.

He was the initiator and organizer of scientific help to construction enterprises; he went several times to the constructions on the Volga-Don and the Kuibyshev Hydroelectric station in order to act as consultant. On his initiative, short courses were organized in Saratov for workers in factory laboratories.

His public lectures devoted to actual scientific and practical problems of analytical chemistry always attracted a wide audience.

L. M. Kulberg died in his prime. L. M. Kulberg will always be a shining example of one ceaselessly working for science and the good of his country, and will always be remembered by those who met this energetic and charming man.

The Most Important Scientific Works of L. M. Kulberg

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ANNOUNCEMENT

The Chemical Sciences Division of the USSR Academy of Sciences wishes to announce that on the 20th of June, 1955 a conference will be held in Moscow which will discuss chemical kinetics and reactivity.

The conference will discuss the present state of knowledge in this field of chemical science and the best ways of developing it in the future. For the sake of convenience the discussions at the conference will be based on reports already published; these are: "Some problems in chemical kinetics and reactivity", Academician N. N. Semenov (Acad. Sci. Press, Moscow-Leningrad, 1954), and two collected reports, "Questions in chemical kinetics, catalysis, and reactivity"(Acad. Sci. Press, Moscow-Leningrad, 1955). The work of the conference will be mainly devoted to short discussions on the above questions.

The Chemical Sciences Section invites workers in research institutes, higher educational establishments, and factory laboratories to take an active part in discussing these reports, and thus further the successful development of the theory of chemical processes.

Applications for tickets for participation in the conference should be sent to the address of the Organizing Committee (Moscow, Bolshaya Kaluzhskaya, 14, Acad. Sci. Chemical Sciences Section, Organizing Committee for the conference on chemical kinetics and reactivity).

USSR Academy of Sciences, Chemical Sciences Division

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